Analytical Abstracts

A monthly publication dealing with all branches of analytical chemistry: issued by the Society for Analytical Chemistry

Volume 8
No. 10, Abstracts 4029 - 4440

October, 1961

Published for the Society by
W. HEFFER & SONS LTD., CAMBRIDGE, ENGLAND

Binding . . .

W. Heffer & Sons Ltd. announce that they are now able to BIND copies of ANALYTICAL ABSTRACTS, in an approved binding case, at a cost of 14/6 per volume. The 12 Parts for 1960 together with Index and remittance for 14/6 should be sent to

W. HEFFER & SONS, LIMITED
HILLS ROAD, CAMBRIDGE

IMPORTANT NOTICE TO SUBSCRIBERS

(Other than Members of the Society)

The Subscription to *Analytical Abstracts*, inclusive of Index, is £5 per annum; and for *Analytical Abstracts* together with *The Analyst* and Indexes is £8 8s. per annum.

The price of single copies of *Analytical Abstracts*, including back numbers, is 10s. 6d. post free.

Analytical Abstracts is available printed on one side of the paper only, suitable for incorporation into reference systems; the cost is £5 7s. 6d. per annum, exclusive of Index.

All further enquiries about subscriptions should be made through the Secretary, the Society for Analytical Chemistry, 14, Belgrave Square, London, S.W.1. Telephone: BELgravia 3258.

a passage
to Holland...

. . . or it could well have been Basle, Cape Town, Manchester, Melbourne, Uppsala or Trail B.C.

In Universities and Industrial Research Laboratories the world over the SP100 Infrared Vacuum Spectrophotometer is providing a combination of high resolution, extreme quantitative accuracy, speed and reliability otherwise unobtainable in one instrument.

Write for the comprehensive brochure giving full details of this remarkable, versatile and powerful spectroscopic tool.

UNICAM

SP 100

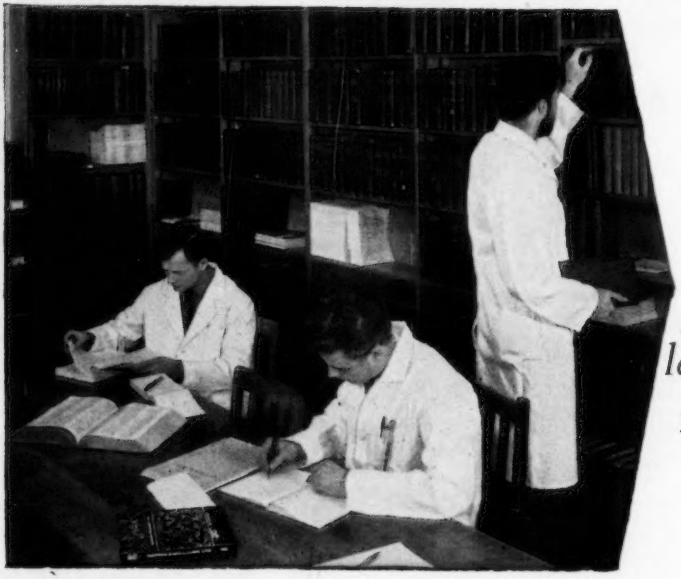
Infrared Spectrophotometer

is the complete answer to the most exacting demands of present day analysis

UNICAM INSTRUMENTS LIMITED · YORK STREET · CAMBRIDGE · ENGLAND

Incidental information

No. 15



Items of interest from our laboratory notebooks

Acid radicles by colorimetry

This method, depending on the liberation from chloranilates of an equivalent amount of highly coloured chloranilic acid, is continually gaining in scope as the appropriate chloranilates become available.

We now prepare and supply from stock:—

Barium chloranilate for **sulphate**

(J. E. Barney and R. J. Bertolacini, *Anal. Chem.* **30**, 202 (1958)).
CODE 1909 Price—5g: 10/9, 10g: 20/-

Mercuric chloranilate for **chloride**

(the above paper and *idem, ibid.* **29**, 1187).
CODE 5541 Price—5g: 10/6, 10g: 19/6

Lanthanum chloranilate for **fluoride**

(K. Hayashi *et al., Talanta*, **4**, 126 (1960)) and for **phosphate** (*idem, ibid.*, **4**, 244 (1960)).
CODE 5002·5 Price—5g: 11/9, 10g: 22/-

For analysis and production

1:10-Phenanthroline, a sensitive reagent that gives a stable colour with ferrous ions, can be used to mask Cd^{2+}, Co^{2+}, Cu^{2+}, Ni^{2+}, Mn^{2+} and Zn^{2+} in the complexometric titration of Pb^{2+} and Al^{3+} with EDTA. (R. Pribil and F. Vydra, *Coll. Czech. Chem. Commun.*, **24**, 3103 (1959) (in German): *Anal. Abs.* 2668 (1960)). It is also a **dryer-catalyst** and, in conjunction with manganese, can shorten the drying time of printing ink on 'acid' papers (W. H. Canty *et al., Ind. Eng. Chem.*, **52**, 67 (1960)). We offer in bulk for industrial use at considerably reduced prices.
CODE 6580 Price—1g: 6/-, 5g: 23/3

Greater selectivity

As the metal indicator Xylenol Orange is used in acid solution, the EDTA titration is unaffected by some common metal ions that do not form EDTA complexes at low pH. Selectivity can be increased still further by using **acetylacetone**, which will mask Fe^{3+}, Al^{3+}, Be^{2+}, Pd^{2+} and UO_2^{2+} in, for instance, the determination of Zn^{2+} or Pb^{2+} (W. Z. Jablonski and E. A. Johnson, *Analyst*, **85**, 297 (1960)).

The above are further examples from the great range of up-to-date reagents made available by Hopkin & Williams Ltd.

H&W TRADE MARK

CHEMICALS

for research, analysis and industry

HOPKIN & WILLIAMS LTD., CHADWELL HEATH, ESSEX, ENGLAND

Branches: London, Manchester, Glasgow — *Agents throughout U.K. and all over the world*

TAS/HW.14

ANALYTICAL ABSTRACTS

1.—GENERAL ANALYTICAL CHEMISTRY

General reviews of progress, reagents and methods of general application.

4029. **Analysis for industry.** W. I. Stephen. *Ind. Chem.*, 1961, **37** (2), 86–88.—The detection of elements (C, H, O, S, halogens, P, As and metals) in organic compounds is discussed. (23 references.) S.C.I. ABSTR.

4030. **Applications of gas chromatography.** I. G. McWilliam (Centr. Res. Lab., I.C.I. of Australia and New Zealand Ltd., Melbourne). *Rev. Pure Appl. Chem.*, 1961, **11** (1), 33–62.—A review, with 349 references.

4031. **The use of new methods in scientific criminology.** G. Machata (Inst. f. gericht. Med., Univ. Wien, Austria). *Arch. Kriminol.*, 1961, **127** (1–2), 1-21.—The analysis of petrol, oil, tar and wax is described. Determination of the aromatic and aliphatic hydrocarbon content of different grades of petrol is possible by gas chromatography and by u.v. and near i.r. spectrophotometry; a preliminary treatment with H_2SO_4 removes olefinic material. Tetraethyl-lead is readily determined colorimetrically, or by flame-photometric measurement at 405·8 mμ, while residues from the distillation of petrol are examined for dyestuffs by thin-layer chromatography. This procedure is also useful for the analysis of bitumens and waxes. P. D. FARR-RICHARD

4032. **Quality of observations. A.S.T.M. Symposium, Atlantic City, N.J., July 1960.** R. B. Murphy and others (Bell Telephone Labs., Inc., New York, N.Y., U.S.A.). *Mater. Res. & Stand.*, 1961, **1** (4), 264–277.—The following papers are included. **The meaning of precision and accuracy,** R. B. Murphy, pp. 264–267. **How to evaluate accuracy,** W. J. Youden, pp. 268–271.—The error in a measurement comprises the systematic error inherent in the procedure, the local systematic error of the laboratory concerned, and the random error. Ways in which these sources can be identified and compensated by planned experiments so as to improve the accuracy are described. **How to evaluate precision,** W. S. Connor, p. 272.—The assessment of the precision of a method by comparing the results of inter-laboratory tests is explained. As an example, the determination of wool in part-wool blankets is described. **The analysis of planned experiments,** M. E. Terry, pp. 273–275.—The analysis of the results of a statistically designed experiment is explained, with reference to the effect of reducing corrosion by evaporating a metal on an electrical element by using 10 elements at 6 different thicknesses of metal. Maximum information is obtained by the control chart method and by the analysis of variance, supplemented by components of variance, multiple comparisons, and analysis of residuals. **General discussion,** pp. 275–277. W. J. BAKER

4033. **Operational statistics in instrumental analysis.** A. B. Calder (Rutherford Coll. of Technol., Newcastle upon Tyne, England). *Appl. Statist.*, 1960, **9** (3), 170–177.—By the use of simple statistical methods, which are described, the cost and labour of calibration procedures in emission spectrography and in flame photometry are substantially reduced. A. R. ROGERS

4034. **Errors of difference determinations.** K. Eckschlager (Inst. Res. Ores, Prague). *Chem. Průmysl*, 1961, **11** (3), 136–137.—By using the general mathematical theory of errors, the most advantageous procedure for the determination of two components (*e.g.*, KCl and NaCl) by indirect analysis is worked out, and the optimum conditions for weighing are given. J. ZÝKA

4035. **Dihydroxymaleic acid in chemical analysis.** N. D. Sadzhaya and V. P. Goguadze. *Soobshch. Akad. Nauk GruzSSR*, 1960, **24** (3), 289–290; *Ref. Zhur., Khim.*, 1961, (1), Abstr. No. 1D15.—Dihydroxymaleic acid (**I**) can be determined by titration with 2,6-dichlorophenolindophenol (sodium salt); with 0·01N-**I** the error is $\geq$ 3·6%. **I** can be used for the spot detection of Ag^+, Hg^{2+} and MoO_4^{2-}. To detect Ag^+, place 1 drop of test soln. on filter-paper and add 1 drop of fresh 0·01N-**I**; in the presence of Ag a dark spot gradually appears. In ammoniacal soln. the reaction is almost instantaneous. The sensitivity is 0·1 to 2 μg of Ag at a limiting dilution of 1 in 5×10^5. Mercury and Bi interfere. Mercury is detected in the same way, with 2 to 3 drops of **I** soln.; a white ppt. gradually forms, slowly turning grey and then black. The reaction is more rapid in ammoniacal soln. The sensitivity is 1 μg of Hg at a limiting dilution of 1 in 5×10^4. Silver and Bi interfere. With MoO_4^{2-} a yellow colour is formed; the reaction is much more rapid if the test soln. is acidified with dil. H_2SO_4. If 1 drop of test soln., 1 drop of conc. H_2SO_4 and 1 drop of 0·01N-**I** are mixed on a watch-glass, a green colour, slowly turning blue, is formed. The sensitivity in each case is 1 μg of MoO_4^{2-} at a limiting dilution of 1 in 5×10^5. C. D. KOPKIN

4036. **Thioformanilide as a precipitant for metal sulphides: a qualitative approach.** M. B. Antia, R. C. Arora and R. P. Bhatnagar (Dept. of Chem., Holkar Coll., Indore, India). *Analyst*, 1961, **86**, 202–203.—Thioformanilide in soln. in ethanol or dioxan serves as a precipitant of the sulphides of metal cations. Owing to formation of a chelate the ppt. is yellowish, but decomposes to form the sulphide either on standing for a few minutes or more rapidly on slight warming. When the mixture is boiled (always necessary with neutral mercury and ammoniacal copper soln.) the sulphide is formed almost instantly. The time required for pptn. is much less than that needed with H_2S, and the reagent has the advantage over thioacetamide that it completely precipitates Cd, Sn^{4+} and Pb. A. O. JONES

4037. Radiometric determination of organic precipitants. H. V. Weiss and M. G. Lai (Naval Radiological Defense Lab., San Francisco). U.S. Naval Radiol. Defense Lab. Rep. TR.440, 1960. 10 pp.—The determination of two organic precipitants, K rhodizonate and 1-nitroso-2-naphthol, is described. The method involves the quant. pptn. of the organic reagent with a radioactive element and isotopic carrier, and the subsequent determination of the activity of the ppt.
NUCL. SCI. ABSTR.

4038. Pyridine derivatives in analytical chemistry. I. The use of copper-substituted pyridine complexes in qualitative analysis. A. Sa and D. B. Budzko (Univ. of Buenos Aires, Argentina). *Rev. Asoc. Bioquim. Argentina*, 1960, **25**, 103–120.—The use of Cu complexes of various substituted pyridines for identifying org. acids (*e.g.*, benzoic and salicylic), and their derivatives, has been examined by using spot tests and tests involving extraction with $CHCl_3$ or microscopic examination of precipitates. The compounds offering most promise were the 3- and 4-picolines and diethylnicotinamide (nikethamide). L. A. O'NEILL

4039. Thoron: an interesting chromogenic agent and chelatochrome indicator. M. B. Johnston, A. J. Barnard, jun., and W. C. Broad (J. T. Baker Chem. Co., Phillipsburg, N.J., U.S.A.). *Rev. Univ. Ind., Santander, Colombia*, 1960, **2**, 137–146 (in Spanish).—A review of the applications of thoron (thoronol), with 109 references.

4040. Problems of blanks in the analysis of trace elements. M. Knížek and J. Provazník (Res. Inst. A. S. Popov, Prague, Czechoslovakia). *Chem. Listy*, 1961, **55** (4), 389–399.—A review is presented with 57 references. J. ZÝKA

4041. The rational basis of volumetric analysis. A. Graire. *Chim. Anal.*, 1961, **43** (2), 53–67; (3), 114–126.—The theory and practice of volumetric analysis as established by Sanfourche in *"Contrôle analytique dans l'industrie chimique minérale"* (Paris, 1936) is summarised and reviewed critically with special reference to the selection and standardisation of soln. used in acidimetry, alkalimetry, argentimetry, manganimetry, chromometry, cerimetry and iodimetry. The preferred French scheme of standardising the different soln. against each other is compared with that recommended by Kolthoff, including the selection and preparation of the primary standards. (70 references.)
W. J. BAKER

4042. Iodimetry in methyl cyanide. J. Desbarres (Lab. Chim. Anal., École Sup. de Phys. et Chim., Paris). *Bull. Soc. Chim. France*, 1961, (3), 502–506.—The stability constant of I_3^- and the normal potentials of the oxidation-reduction systems I_3^-/I^- and I_2/I_3^- in methyl cyanide have been determined. The possibilities of using this system for potentiometric titration are discussed.
G. BURGER

4043. 'Ligand exchange': a novel separation technique. F. Helfferich (Shell Development Co., Emeryville, Calif., U.S.A.). *Nature*, 1961, **189**, 1001–1002.—Compounds that form complexes or adducts with metal ions can be separated by ligand exchange, with standard chromatographic procedures. The ligands (NH_3, amines, polyhydric alcohols, olefins, amino- and organic-acid anions) are adsorbed from soln. or gases on to a column of ion-exchange resin containing, *e.g.*, Cu^{2+}, Cu^+, Ni^{2+}, Ag^+ or Co^{3+}, thus forming strong complexes with the metal or displacing other ligands that have previously complexed the metal, the latter always remaining in the ion exchanger. Advantages claimed over conventional chromatography include stronger and more selective adsorption, higher specificity of complex formation ensuring sharper separations, and more flexibility in adjusting conditions to achieve the required separation. As examples (*i*) from 10 litres of soln. there is 100% adsorption of 10 p.p.m. of most aliphatic amines by > 1 g of resin (Cu^{2+} or Ni^{2+} form), and (*ii*) separation factors > 100 are achieved with NH_3 and a diamine. Some general applications and the effects of other cations in the sample soln. and of the co-ordination valencies of the ligands are discussed briefly. W. J. BAKER

See also Abstracts—**4052**, Use of dilituric acid. **4070**, Use of 5-hydroxyimino-4-imino-1,3-dimethylalloxan. **4228**, Analysis of mixtures of complexans.

2.—INORGANIC ANALYSIS

General, determination of elements (arranged in the order of the Periodic Table), analysis of minerals and inorganic industrial products.

4044. Extraction behaviour of metal acetylacetonates. Tsunenobu Shigematsu and Masayuki Tabushi. *Bull. Inst. Chem. Res. Kyoto Univ.*, 1961, **39** (1), 35–42.—Curves for the extraction with $CHCl_3$, at pH from 2 to 12, of the acetylacetonates of the following metals are shown and discussed—Al, Be, Cd, Ce, Co, Cu, Fe^{III}, Ga, Hf, In, Pb, Mg, Mn, Ni, Sr, U, Y and Zn. Max. recovery of the complex increases with increasing ionic or ionisation potential of the metal, whilst the pH value for unit partition ratio decreases linearly with increasing ionic potential.
W. J. BAKER

4045. Analytical application of the oxidation of EDTA with permanganate. M. T. Beck (Inst. of Inorg. and Anal. Chem., Univ., Szeged, Hungary). *Chemist Analyst*, 1961, **50** (1), 14–15.—At 60° and in H_2SO_4 or $HClO_4$ medium, EDTA is oxidised by $KMnO_4$, one mole consuming 6 equiv. of oxidant; this enables EDTA to be determined with an error of $< \pm 1\%$. When EDTA is complexed with a metal ion it is not oxidised so that, with an excess of Bi^{3+} to complex the EDTA, H_2O_2 can be determined in the presence of EDTA stabiliser. The indirect determination of metal ions can be accomplished by adding an excess of standard EDTA soln. and titrating the free complexan. In this way Bi and Fe^{III} are determined with errors of $< \pm 1\%$ and $\pm 2\%$, respectively. Common bi- and ter-valent ions (except Cr^{III} and Hg^{II}) do not interfere. The simultaneous determination of Bi and Fe is also possible. Detailed procedures are given. J. H. WATON

4046. Chromatography of some cations by means of paper treated with a liquid anion-exchanger. C. Testa (Lab. C.I.S.E., Milan, Italy). *J. Chromatography*, 1961, **5** (3), 236–243 (in English).—When filter-paper is treated with a long-chain tertiary amine, *e.g.*, tri-n-octylamine, it will behave like an anion-exchange resin, selectively

extracting the anionic complexes of many cations from acid solutions. Separations have been satisfactorily obtained of, *e.g.*, Fe, Co and Ni, from one another, and of Zr from Hf, when the HCl-complexed cation is chromatographed on this treated paper. Other examples of this type of separation are given. The technique also provides an easy way of isolating traces of complexed elements from large amounts of other cations not retained by the amine. G. P. MITCHELL

4047. **Gas - liquid chromatography of volatile metal halides.** R. A. Keller (Dept. of Chem., Univ. of Arizona, Tucson, U.S.A.). *J. Chromatography*, 1961, **5** (3), 225–235 (in English).—The literature on the gas chromatography of volatile metal compounds is reviewed and experimental details, with results, are given of an investigation on the gas chromatography of $SnCl_4$, $TiCl_4$, $NbCl_5$ and $TaCl_5$ at 100°, 150° and 200°, with squalane, n-octadecane, silicone oil, paraffin wax and Apiezon grease as partitioning agents, supported on Red Chromosorb. Difficulties of the technique are pointed out and suggestions for further work are given. (16 references.) G. P. MITCHELL

4048. **Cation-exchange elution of metal chlorides by hydrochloric acid.** C. K. Mann and C. L. Swanson (Dept. of Chem., State Univ., Tallahassee, Fla., U.S.A.). *Anal. Chem.*, 1961, **33** (3), 459–462.—The effects of resin cross-linkage (2 to 16% of divinylbenzene) and eluent concn. on the elution of Mn^{2+}, Fe^{3+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Fe^{2+} and Hg^{2+} from a column (4 to 8 cm × 1 sq. cm) of Dowex 50-W with 0·5M to 12M-HCl are reported and discussed in respect of optimum conditions for complete separations. With approx. equiv. concn. of components, mixtures of these elements can generally be resolved by elution with 0·5M to 1M-HCl at a rate of flow of ≃ 0·5 ml per sq. cm per min. through a 12% cross-linkage resin. Thus, Hg^{2+} are separated from all the other ions by elution with 0·5M-HCl, Cd^{2+} are separated from all ions except Hg^{2+} by elution with M-HCl, Zn^{2+} are separated preferentially from Ni^{2+}, Mn^{2+}, Fe^{2+} and Mg^{2+} by 2M to 4M-HCl, whilst Cu^{2+}, Ni^{2+}, Cd^{2+} and Hg^{2+} are each separated from Fe^{3+} by elution with 12M-HCl. If a 7-cm column is used, Zn^{2+} can be separated from Fe^{3+} in ≃ 30 min.; Zn^{2+} cannot be separated from Cu^{2+}, whilst Cu^{2+}, Ni^{2+}, Mn^{2+}, Fe^{2+} and Fe^{3+} are not readily separated. W. J. BAKER

4049. **Infra-red spectrometry of inorganic substances.** V. V. Klimov. *Zavod. Lab.*, 1961, **27** (3), 292–294.—A review, with 32 references, is presented. G. S. SMITH

4050. **Flame-photometric determination of some rare metals which do not radiate in the flame.** N. S. Poluéktov and L. I. Kononenko. "Spektr. Anal. v Tsvet. Metall.", M., Metallurgizdat, 1960, 38–42: *Ref. Zhur., Khim.*, 1961, (1), Abstr. No. 1D51. —It is shown that salts of Zr, Hf, Ti^{IV}, V^{V}, Mo^{VI} and U^{VI}, when present in soln. with salts of Ca and Sr, reduce the intensity of radiation of the Ca and Sr in coal-gas - air or acetylene - air flames. With Zr and Hf, the reduction in the intensity of the Ca radiation is the same in both flames; with Ti, the Ca radiation is reduced more in coal-gas - air flames, and the same is found with V^{V} with respect to the Ca and Sr radiation; with Mo the reduction of intensity of the Ca and Sr radiation is slight in the acetylene - air flame, but pronounced in the coal-gas - air flame. Similar effects are found in the quenching of the Ca radiation in the presence of U. By using two atomisers it is shown that the observed reduction of intensity is due to the formation, by evaporation of the drops of aerosol in the flame, of compounds of low volatility between Ca or Sr and the added metal. From the relationship between the degree of quenching of the Ca and Sr radiation and the concn. of added metal, it is concluded that the compounds formed between Ca and Ti, V and Ca and Sr, and U and Ca contain the added metal and Ca or Sr in the ratio 1:1. The degree of quenching can be used for the indirect determination of the added metal. C. D. KOPKIN

4051. **Use of oscillographic polarography in quantitative analysis. XIV. Micro-analytical determinations with the hanging mercury drop electrode.** R. Kalvoda and C. C. Stockmannová (Polarographic Inst., Acad. Sci., Prague, Czechoslovakia). *Chem. Listy*, 1961, **55** (4), 477–481.—A drop of mercury suspended on a silver wire (Micka, *Ibid.*, 1961, **55**, 474) as indicator electrode and a special oscillopolarographic apparatus was used for the determination of ≃ 0·0001% of Cu and Pb in calcium carbonate and 0·001% of Cu and Pb and 0·01% of Cd in zinc oxide. *Procedures:* (*i*) *With calcium carbonate*—Dissolve the sample (5 g) in electrolytically purified acetic acid (25%) (25 ml), adjust the pH to 5·0 to 5·4 with more acetic acid and dilute the soln. with H_2O to 50 ml. Electrolyse an aliquot (5 ml) for 3 min. at 3 mA, connect the electrode with the circuit for the a.c. polarograph and simultaneously register the oscillopolarographic curve photographically. (*ii*) *With zinc oxide*—Dissolve the sample (2 g) in acetic acid (25%) (15 ml), adjust the pH to 5·0 to 5·4 and dilute the soln. to 50 ml. To an aliquot (2 ml) add 0·5M-EDTA (disodium salt) and electrolyse for 5 min. at 1·2 mA. Then dissolve the zinc amalgam for 1 min. at − 1·12 V and polarise the electrode for 10 sec. with continuous current and register the oscillopolarographic curve. In both cases compare the depth of the incision with standard curves. Average errors of ⩾ ± 20% were obtained. J. ZÝKA

4052. **Thermogravimetric determination of magnesium, potassium and lead by precipitation with dilituric acid.** A. Berlin and R. J. Robinson (Dept. of Chem., Univ. of Washington, Seattle, U.S.A.). *Anal. Chim. Acta*, 1961, **24** (3), 224–234 (in English).—The stable hydrates or anhyd. salts of Mg, Pb and K with dilituric acid (5-nitrobarbituric acid) (**I**) have been isolated and studied thermogravimetrically. Conditions for the use of **I** (or of trimethylamine dilituric for K) as a gravimetric reagent have been established. P. D. PARR-RICHARD

4053. **Paper-chromatographic separation of bismuth, cadmium, copper, lead and mercuric mercury.** V. K. Mohan Rao (Centr. Drug Res. Inst., Lucknow). *J. Sci. Ind. Res., India, B*, 1961, **20** (3), 109–111.—A chromatographic method for separating group 2A metals with 0·01N-HCl or 0·05N-H_2SO_4 is given. Cadmium, Cu and Hg^{II} can be separated in 0·05N-H_2SO_4 medium. Lead interferes in the separation of Cu from Hg and must first be pptd. with conc. H_2SO_4. R_F values in different mixtures are studied, also the influence on the separation of variations in concentration of solvent and cation. Coloured bands developed with NH_3 - H_2S are stable, except that CuS is slowly

oxidised to $CuSO_4$. Bands obtained with organic solvents and developed with NH_3 - H_2S vapour fade after a time. The mechanism of the separation in inorganic solvents is thought to be by adsorption rather than by partition. R. PRESSER

4054. **Analysis of indium - arsenic - selenium alloys.** G. A. Kalyuzhnaya and A. S. Khalonin (Leningrad State Univ.). *Zavod. Lab.*, 1961, **27** (3), 261–263.—A soln. in H_2SO_4 (1:4) of $\simeq$ 100 mg of In, As and Se is treated with SO_2 and heated on a boiling-water bath until the pptd. Se is black. The ppt. is collected on a sintered-glass filter, washed with 0·5N-H_2SO_4, hot water and ethanol, then dried at 105° and weighed. The filtrate is heated to remove SO_2 completely, and evaporated to a vol. of 70 to 80 ml. It is then treated with 20 ml of HCl and 1 to 2 drops of methyl orange soln. and the As is determined by titration with 0·1N-$KBrO_3$. The titrated soln. is neutralised with aq. NH_3 and a small excess is added. The ppt. is collected and washed with hot water containing a few drops of aq. NH_3, and then dissolved in a slight excess of 0·5N to 1N-H_2SO_4. After addition of hydroxyammonium chloride and excess of a standard soln. of EDTA (disodium salt), the soln. is neutralised with aq. NH_3, heated to boiling and cooled, treated with 10 ml of a buffer soln. (pH 10) and Eriochrome black T, and titrated with $ZnSO_4$ soln. to a violet end-point to give the content of In. G. S. SMITH

4055. **Catalysts for cerium(IV) oxidimetry. Determination of phosphite, hypophosphite, tellurium and mercury.** G. G. Guilbault and W. H. McCurdy, jun. (Princeton Univ., N.J., U.S.A.). *Anal. Chim. Acta*, 1961, **24** (3), 214–218 (in English).—Rapid oxidation by Ce^{4+} in the presence of Mn^{2+} and Ag^+ is used to determine Te, Hg^+, HPO_3^{2-} and $H_2PO_2^-$. *Procedure for HPO_3^{2-}, $H_2PO_2^-$ and Te*—To a soln. of 10 to 100 mg of HPO_3^{2-} or 5 to 35 mg of $H_2PO_2^-$ add 2 ml of soln. *A* [1·2 ml of 50% $Mn(NO_3)_2$ soln. and 5 g of $AgNO_3$ in 100 ml of M-$HClO_4$], 5·5 ml of conc. H_2SO_4 per 100 ml and a 70 to 150% excess of Ce^{4+}. Heat at 100° for 7 to 10 min., cool, add 10 ml of conc. H_2SO_4 and titrate with Fe^{2+}, with ferroin as indicator. For soln. containing Te (5 to 60 mg), add 1 ml of soln. *B* [2·8 ml of 50% $Mn(NO_3)_2$ soln. and 3 g of $AgNO_3$ in 250 ml of M-$HClO_4$], 17 ml of 72% $HClO_4$ soln. per 100 ml and a 50 to 150% excess of Ce^{4+}. Heat at 95° until the soln. is cherry-red, then cool and proceed as described above. *Procedure for Hg^+*—Heat a mixture of Hg^+ soln. (50 to 400 mg), 17 ml of 72% $HClO_4$ per 100 ml and 1 ml of soln. *B* to boiling. Titrate with $Ce(ClO_4)_4$ soln., cool to 50° to 60°, add 2 drops of nitroferroin indicator and complete the titration. P. D. PARR-RICHARD

4056. **Direct ultra-micro spectrophotometry of spots of cobalt, copper and zinc on paper.** P. Heyndryckx (Lab. de Rech. des Usines Sovirel). *Chim. Anal.*, 1961, **43** (3), 127–135.—From 0·1 to 3 μg each of Co, Cu and Zn can be determined to within 0·1 to 0·3% in $\simeq$ 90 min. by direct Beckman spectrophotometry at 850 mμ of the entire surface of the spots obtained (preferably by chromatographic separation) on Whatman No. 4 paper. The reagents used are 2-nitroso-1-naphthol for Co, dithio-oxamide in acetone for Cu, and dithizone for Zn. The reproducibility and accuracy depend on the careful standardisation of the paper and quant. control of the chromatographic separation. Optimum conditions are discussed. W. J. BAKER

4057. **Chelatometric titrations in the presence of tungsten and molybdenum.** E. Lassner and R. Scharf (Metallwerk Plansee A.-G., Reutte, Tirol, Austria). *Chemist Analyst*, 1961, **50** (1), 6–7.—With tartrate, F^-, PO_4^{3-} and occasionally H_2O_2 as masking agents, many metals (except Ti, Zr, Hf, Th and U) can be titrated successfully with EDTA in the presence of W; these masking agents are unsuitable for titrations in the presence of Mo. Diaminocyclohexanetetra-acetic acid (**I**) forms more stable complexes with metals than does EDTA, but the rate of complex formation is frequently slow. With W and Mo, **I** forms only weak complexes, if at all. Thus cations can be titrated with **I** and the copper - PAN indicator system in the presence of excess of W and Mo without the addition of a masking agent. Conditions are summarised for the determination of Ca, Mg, Cd, Zn, Cu, Ni, V and Mo with EDTA in the presence of W, suitably masked, and for the determination of Cu, Ni, Fe, Zr and Ti with **I** in the presence of W and Mo. J. H. WATON

4058. **Determination of gases in metals by means of micro-analysers.** L. Moreau and J. Talbot (Lab. de Vitry du Centre Nat. de Rech. Sci., France). *Bull. Soc. Chim. France*, 1961, (1), 148–153.—Apparatus and methods are described for the determination of O as CO_2, of C as CO_2, and of H as hydrogen gas. *Procedure for O*—After outgassing the apparatus, the electrolytically polished sample is melted under vacuum in a graphite crucible by an induction heater and the CO evolved is held between two mercury cut-offs; O is admitted to the space between the cut-offs and the CO is converted into CO_2 by means of a platinum spiral. The CO_2 formed is condensed in a liquid-nitrogen trap. The uncondensed gases (including excess of O) are then pumped out and the CO_2, after being allowed to evaporate, is measured in a manometer. *For C*—The metal is heated in an atmosphere of O in a platinum crucible, the CO_2 formed is condensed in a trap, and determined manometrically as described above. *For H*—Samples are heated by means of an outgassed iron ring in a quartz crucible and tube, and after all possible gases have been condensed in a liquid-nitrogen trap the H is pumped (if necessary through a palladium tube) by a mercury diffusion pump into a McLeod gauge. The precautions necessary for outgassing, cleaning and calibration are described. E. J. H. BIRCH

4059. **Determining trace impurities in grade-A helium.** C. G. Kirkland, L. W. Brandt and W. M. Deaton (Bureau of Mines, Washington, D.C.). *Rep. Invest. U.S. Bur. Min.*, 1960, No. 5644, 15 pp.—An apparatus for determining trace impurities in helium (99·995% pure) is described, in which the impurities are concentrated by freezing them out in a coil-and-trap assembly cooled by liquid helium. Samples of the condensate are analysed with a mass spectrometer. NUCL. SCI. ABSTR.

4060. **Spectrophotometric determination of microgram quantities of vaporisable water from solids using the Karl Fischer reagent.** D. A. Otterson (Lewis Res. Center, Nat. Aeronautics and Space Admin., Cleveland, Ohio, U.S.A.). *Anal. Chem.*, 1961, **33** (3), 450–453.—The colorimetric method described, which has a sensitivity of 0·5 μg at 475 mμ, is based on the measurement of the change in extinction when the Karl Fischer reagent reacts with H_2O. Details are given of an apparatus

for transferring the H_2O from a solid sample to a collector and then to the reagent. Beer's law is obeyed and results on 11 samples of $BaCl_2.2H_2O$ containing 11 to 26 μg of H_2O show an average error of $\pm$ 2 μg. Some of the difficulties encountered in the exclusion of extraneous H_2O are described. C. B. BAINES

4061. **Analysis of water and deuterium oxide mixtures by infra-red spectroscopy. Determination of molecular extinction coefficients.** M. Ceccaldi (Centre d'Études Nucléaires, Saclay, France). *Rev. Univ. Min.*, 1959, **15** (9), 7 pp. (in French).—The various conditions for the i.r. analysis of H_2O - ^2H_2O mixtures are briefly recapitulated. An absolute method for analysing these mixtures is proposed, and the results obtained by i.r. spectroscopy are compared with those obtained by nuclear resonance. Details of the apparatus used (a conventional spectrometer for laboratory determinations and an i.r. photometer for continous analysis) are given. NUCL. SCI. ABSTR.

4062. **Determination of tritium in water and urine. Liquid scintillation counting and rate-of-drift determination.** F. E. Butler (Savannah River Plant, E.I. du Pont de Nemours & Co., Inc., Aiken, S.C., U.S.A.). *Anal. Chem.*, 1961, **33** (3), 409–414.—The use of an improved scintillation mixture and disposable, low-background, polyethylene vials enables untreated urine samples to be assayed at ^3H levels of 1 μC per litre after a 1-min. count. The lower limit of detection of ^3H in water is 0·005 μC per litre, and 0·05 μC per litre can be determined with a relative standard deviation of $< 10\%$ after a 30-min. counting period (20 samples). The results are comparable with those of a second method, in which a vibrating-reed electrometer is used. This procedure requires less expensive equipment and enables 6 samples per day to be assayed. A 12 to 14-fold increase in concn. is obtained by a two-day electrolysis, and the ^3H is determined by either of the two described methods; ^3H at levels of 5×10^{-4} μC per litre of water can thus be determined. C. B. BAINES

4063. **Spectrophotometric determination of trace amounts of calcium in sodium. Visible and ultra-violet methods using sodium naphthalhydroxamate.** D. K. Banerjee, C. C. Budke and F. D. Miller (U.S. Industrial Chemicals Co., Cincinnati, Ohio). *Anal. Chem.*, 1961, **33** (3), 418–421.—In the method, which is specially applicable to reactor-grade sodium (max. limit of Ca 15 p.p.m.), the Ca is pptd. from the sample soln. (NaCl) with a dil. soln. of Na naphthalhydroxamate at $\simeq$ 100°. The mixture is cooled and centrifuged, and the Ca naphthalhydroxamate is then collected, washed and dissolved in 0·1M-EDTA (disodium salt) at $\simeq$ 80° to release an equiv. amount of intensely coloured naphthalhydroxamate ions, the colour intensity of which is proportional to the concn. of Ca and is measured at 339 mμ and 25° in 5-cm borosilicate cells, with H_2O as reference soln. The use of the peak at 339 mμ ensures a tenfold sensitivity over that attained at 410 mμ. An indirect photometric procedure that saves much time and gives higher accuracy for low concn. (1 to 50 μg per 25 ml) is also described. Iron, Al, Cu, Mn, Ba, Mg, K, Sn, Ti, V, Cl^-, OH^-, SO_4^{2-}, F^-, NO_3^-, PO_4^{3-} and oxalate do not normally interfere; a max. of $\simeq$ 40 μg of Sr can be tolerated. The method can be extended to other materials. W. J. BAKER

4064. **Determination of trace nickel and copper in sodium hydroxide solutions and in sodium hypochlorite solutions.** F. Mains and R. E. Raggett (Javex Co. Ltd., Toronto, Ontario, Canada). *Chemist Analyst*, 1961, **50** (1), 4–6.—Colorimetric procedures are described for determining Cu and Ni in the range 0·1 to 1·0 p.p.m. to within 0·01 p.p.m. The Ni is determined as the furil α-dioxime complex in $CHCl_3$, after Cu has been removed with ammoniacal tartrate soln. The Cu is determined as the neocuproine complex in butanol in the presence of Ni. The sensitivities of the determinations are—for Ni, $\not<$ 0·1 μg at a dilution of 1 in 5×10^8 (w/w) and, for Cu, $\not<$ 0·15 μg at a dilution of 1 in $3{\cdot}3 \times 10^8$ (w/w). J. H. WATON

4065. **Conductimetric determination of small amounts of alkali carbonate in admixture with excess of hydroxide.** Z. Hošťálek and F. Kůtek (Dept. Inorg. Technol., Inst. Chem. Technol., Prague). *Chem. Průmysl*, 1961, **11** (4), 177–180.—The graphical method described was suitable for the titration with HCl of samples containing a large excess of hydroxide. Instead of the end-point, the displacement of the entire limb of the titration curve, after the end-point has been passed, is determined. The method depends on the fact that the conductivities of small amounts of alkali carbonates are nearly the same as those of the chlorides formed therefrom during the titration. J. ZÝKA

4066. **Flame-photometric determination of traces of sodium and potassium in the presence of other metals, and methods for overcoming some interferences.** R. N. P. Farrow and A. G. Hill (The British Drug Houses Ltd., Lab. Chem. Div., Poole, Dorset, England). *Talanta*, 1961, **8** (2–3), 116–128.—Sodium and K can be determined directly as impurities in soln. containing Al, Be, Bi, Cd, Pb, Mg, Mo, Sn, Ag and Zn, by using a simple flame photometer with optical filters. Erratic results are obtained in the presence of W although it does not interfere directly. The interference of Ca, Sr and Ce can be suppressed by the addition of a large excess of $Al(NO_3)_3$; Cr^{VI} and Mn^{VII} interfere, but can be removed by passing the soln. through a column of Amberlite IRA-400 resin; U^{VI} can be removed similarly, as the complex anion $[UO_2(SO_4)_n]^{2-2n}$; Mn^{II}, Ni, Co, Cr^{III} and Fe can be removed by passing the soln. through a column of Amberlite IRA-400 in the EDTA form. R. M. ROWLEY

4067. **Dimethyl yellow as adsorption indicator in the indirect determination of potassium with tetraphenylborate.** R. Geyer and K. Chojnacki (Inst. f. Anal. Chem., Tech. Hochsch. f. Chem., Leuna-Merseburg, Germany). *Z. anal. Chem.*, 1961, **179** (6), 409–415 (in German).—Potassium is determined by adding an excess of sodium tetraphenylborate at pH 3 to 5 and determining the excess by back-titration with $TlNO_3$. *Procedure*—Treat the soln. (10 to 30 mg of K^+) with 0·05M-sodium tetraphenylborate (preparation described) (20 ml) in a 100-ml flask. Dilute to the mark, set aside for 10 min. and filter. Dilute the filtrate (50 ml) to $\simeq$ 200 ml in a 300-ml conical flask and add ethyl acetate (20 ml) and mixed indicator [100 mg of dimethyl yellow plus 130 mg of Nile Blue (C.I. Basic Blue 12) in 100 ml of ethanol] (8 drops). Add Na acetate soln. (10%) dropwise till the colour changes from violet to green. Then titrate with 0·05M-$TlNO_3$, with continual shaking. The

colour, which is bluish-red as soon as some thallium tetraphenylborate is pptd., becomes bluish-green at the end-point. The $TlNO_3$ soln. is standardised against pure KCl. A systematic error of $\simeq -4\%$ was corrected by the use of an empirical factor. Large amounts ($\simeq 0{\cdot}5$ g) of foreign cations (*e.g.*, Na, Mg, Ca, Al) make the end-point less sharp.

G. RUSSELL

4068. **Flame-photometric determination of rubidium and caesium [in mica].** J. Dvořák (Res. Inst. Inorg. Chem., Ústí nad Labem, Czechoslovakia). *Chem. Průmysl*, 1961, **11** (3), 122–126.—*Procedure*—Treat 1 g of the finely powdered sample in a platinum dish with H_2SO_4 (1:1) (5 ml) and HF (10 ml) and evaporate on a sand bath to fuming. If necessary, repeat the evaporation, always with 10 ml of HF. Then dilute with H_2O to 100 ml. Measure the emission of Rb or Cs in a 10-ml aliquot, in an oxy-hydrogen flame, at 7948 A or 8521 A, respectively. The method is suitable for the determination of 5 to 200 p.p.m. of Rb and 10 to 200 p.p.m. of Cs, with an error $\not> 10\%$. An excess of Na, K, Li, Ca, Fe, V, SO_4^{2-} or Cl^- does not interfere. The results were evaluated by the method of standard addition and a calibration curve.

J. ZÝKA

4069. **Use of sym.-diphenylcarbazide in the determination of copper in condensates.** M. Mrkva and M. Janáčková (NHKG, Ostrava, Czechoslovakia). *Chem. Průmysl*, 1961, **11** (3), 139–140.—*Procedure*—Titrate the sample (5 to 80 μg of Cu per litre) (100 ml) with 0·01N-NaOH to phenolphthalein till the soln. is alkaline (*a* ml), then neutralise with 0·01N-HCl (*b* ml). To another portion of the sample (100 ml) add the NaOH soln. required for neutralisation ($a-b$ ml), benzene (20 ml exactly) and sym.-diphenylcarbazide (1,5-diphenylcarbohydrazide) soln. (0·2% in 50% ethanol). Shake for 3 min., set aside for 3 to 5 hr. and measure the extinction of the benzene layer at 545 mμ. The error is 1 μg of Cu per litre. Iron (< 2 mg per litre) does not interfere.

J. ZÝKA

4070. **Analytical use of 4-imino-1,3-dimethylalloxan 5-oxime. I. Determination of copper.** K. Burger (Inst. of Inorg. and Anal. Chem., L. Eötvös Univ., Budapest, Hungary). *Talanta*, 1961, **8** (2–3), 77–84 (in English).—The reagent forms a 1:1 complex with Cu^{2+} in neutral or slightly alkaline soln. The grass-green complex absorbs strongly at 382 mμ, but the absorption of the reagent is negligible at this wavelength. In Britton and Robinson's buffer soln. (pH 8) containing 0·1% of NH_4Cl the extinction is proportional to Cu^{2+} concn. in the range 1 to 13 mg per litre. It is possible to determine 8 mg of Cu^{2+} per litre with an error of $\pm 3\%$ in the presence of a large excess of Hg^{2+}, Pb^{2+}, Bi^{3+}, Mn^{2+}, Zn^{2+}, Cd^{2+}, Ba^{2+}, Fe^{2+}, Al^{3+}, Ca^{2+}, Mg^{2+}, Na^+ or Sb^{3+}. Small amounts of Co, Pd, Ni or Fe^{2+} interfere. A method is given for the preparation of the reagent.

R. M. ROWLEY

4071. **Colorimetric determination of copper by means of oxalyldihydrazide and acetaldehyde. Supplementary note.** R. Capelle. *Chim. Anal.*, 1961, **43** (3), 111–113.—The validity of the colorimetric determination of Cu in steel, cast iron and other metals with oxalyldihydrazide in the presence of acetaldehyde (**I**) (*cf. Anal. Abstr.*, 1960, **7**, 4125) is confirmed. The deep-violet complex with Cu^{2+} is stable for 72 hr. and the intensity is constant between pH 8·5 and 10, but decreases with increasing loss of **I** during the addition and mixing of the reagents. The max. error from this cause is $\simeq -1{\cdot}3\%$, but is minimised by cooling the **I** initially to $\simeq 5°$ and conducting the subsequent operations at the same temp., adding **I** slowly and in small quantities at a time. Formaldehyde gives a more intense coloration than does **I**, but propionaldehyde, butyraldehyde, benzaldehyde or salicylaldehyde cannot be used instead of **I**.

W. J. BAKER

4072. **Cerimetric determination of copper.** T. N. Bondareva. *Izv. Výssh. Ucheb. Zavedenií, Khim. i Khim. Tekhnol.*, 1960, **3** (3), 416–417; *Ref. Zhur., Khim.*, 1961, (1), Abstr. No. 1D65.—The determination of small amounts of Cu is based on the reduction of Cu^{2+} to Cu^+ in a bismuth reductor, reduction of Fe^{3+} to Fe^{2+} by the resulting Cu^+, and titration of Fe^{2+} with a Ce^{4+} soln. To determine Cu in metallic nickel, dissolve 1 g of sample in 7 ml of HNO_3 (1:1), evaporate, add 10 ml of conc. HCl and remove the SiO_2. To the filtrate add 5 ml of 3% H_2O_2, boil for 10 min. to destroy excess of H_2O_2, add aq. NH_3 (2:1) dropwise to the formation of dark-blue complex salts, heat without boiling for 1 to 2 min., and filter. Collect the filtrate in a 200-ml flask, add conc. HCl to destroy the complexes and 20 ml in excess, and make up to vol. Pass 20 ml of this soln. through a bismuth reductor into 0·02N-Fe^{3+} (20 ml), wash the reductor with N-HCl (3 × 5 ml), and titrate the Fe^{2+} with 0·01N-$Ce(SO_4)_2$ in the presence of 2 drops of *N*-phenylanthranilic acid soln. Run a blank simultaneously.

C. D. KOPKIN

4073. **Spectrophotometric micro-determination of copper and iron in a single aliquot.** B. Zak, G. A. Cavanaugh and L. A. Williams (Path. Dept., Coll. of Med., Wayne State Univ., Detroit, Mich., U.S.A.). *Chemist Analyst*, 1961, **50** (1), 8–9.—The substitution of 2,4,6-tripyridyltriazine (**I**) for bathophenanthrolinedisulphonate as the reagent for Fe improves the resolution of the colour complexes previously described by Zak (*Anal. Abstr.*, 1959, **6**, 268); bathocuproinedisulphonate (**II**) is retained as the reagent for Cu. *Procedure*—The sample soln. is diluted with an equal vol. of 10% trichloroacetic acid soln. and 4 ml is transferred to a 1-cm cell; satd. Na acetate soln. (1 ml) and 10 to 20 mg of ascorbic acid are added and the extinction of the soln. is read at 485 mμ against that of a blank of 5% trichloroacetic acid soln. (reading R_1). To both sample and blank, 0·1 ml of a 0·4% soln. of **II** (disodium salt) in 4% acetic acid is added, and the extinctions of the sample soln. are read at 485 and 600 mμ against those of the blank (readings R_2 and R_3, respectively). To each soln. is added 0·1 ml of a 0·4% soln. of **I** in 4% acetic acid, and the extinction of the sample soln. is read at 600 mμ against that of the blank (reading R_4). The corrected extinction due to the Cu complex of **II** is $(R_2 - R_1)$, and that due to the Fe complex of **I** is $(R_4 - R_3)$. Calibration curves must be plotted. By this method, Cu and Fe in the range 0·25 to 3·0 mg per litre can be determined in the same aliquot, a range of concn. which would include pathological extremes in biological systems such as blood serum.

J. H. WATON

4074. **Precipitation of transition-metal ions with metal and semi-metal sulphides. The separation of copper from lead with cadmium sulphide.** M.

Ziegler (Anorg.-Chem. Inst., Univ., Göttingen, Germany). *Z. anal. Chem.*, 1961, **180** (1), 4–8 (in German).—Use is made of the differing solubilities of metal sulphides for various separation schemes. Thus, in weakly acid soln., CdS will precipitate Cu, Bi, Ag, Hg, Au and Pd, but not Pb or Tl; Tl_2S will precipitate Pb but not Cd; PbS will precipitate Ag but not Cu in the cold (Cu will precipitate on boiling); As_2S_3 will precipitate Ag and Bi, but not Cu, Pb or Cd; CuS will precipitate Au^{3+}, Bi, Pd, Hg and Ag, but not Pb or Cd. *Procedure for separating Cu and Pb*—To the test soln. (100 ml) containing the metals as nitrates and free HNO_3 (1 ml) add CdS (800 mg) and stir vigorously for 15 min. Filter on a sintered-glass filter (1G4), wash the ppt. with 5% NaOH soln. (10 ml) and water. Transfer the crucible to a 150-ml beaker, add water (10 to 20 ml) and HNO_3 (2 to 4 ml) and heat to dissolve the ppt. Wash the crucible and dilute the soln. to 50 ml. For the range 3 to 30 mg of Cu, determine the Cu with glycine at 537 mμ (*Anal. Abstr.*, 1959, **6**, 2038). For the range 0·3 to 3 mg of Cu, determine with violuric acid at 415 mμ (*Anal. Abstr.*, 1959, **6**, 2871). The Pb in the filtrate may be determined with EDTA. The procedure was successful with up to a 10,000-fold excess of Pb, a 350-fold excess of Co, a 1000-fold excess of Ni and a 20-fold excess of Fe^{3+}. The error in 38 determinations (1 to 25 mg of Cu) was within ± 1%. G. Russell

4075. **Rapid estimation of copper in type-metals and lead-base Babbitt metals.** J. Brinn. *Metallurgia, Manchr*, 1961, **63**, 52.—The sample (1 g) is dissolved in conc. H_2SO_4 (7 ml) and heated until the ppt. formed is light grey. Water (10 ml) is added, with stirring, followed by conc. HCl (5 ml) and the soln. is boiled until the ppt. is white. The soln. is diluted with water (30 ml), neutralised with conc. aq. NH_3 and acidified with acetic acid. A gum acacia soln. [2% in aq. glycerol (1:1)] (5 ml) is added, followed by 4 ml of 0·33% ethanolic dithio-oxamide soln. The soln. is filtered through Whatman No. 31 paper and the colour is measured at 650 mμ. S.C.I. Abstr.

4076. **Use of methyl violet in the determination of small amounts of antimony in copper.** A. G. Kon'kov. *Trudy Stalingrad. Sel.-Khoz. Inst.*, 1960, **8**, 59–64; *Ref. Zhur., Khim.*, 1961, (1), Abstr. No. 1D128.—*Procedure*—Dissolve 2 to 4 g of the sample in HNO_3 (1:4), evaporate to a small vol., dilute to 25 to 30 ml, add aq. NH_3 till a turbidity appears, re-dissolve this with HNO_3 (1:4), add 5 ml of 10% $MnSO_4$ soln. and 2 ml of 5% $KMnO_4$ soln. and boil; after 3 to 5 min. add a further 2 ml of $KMnO_4$ soln. and boil for 5 to 10 min. Filter off the pptd. MnO_2 containing co-pptd. Sb, and wash it with hot water. Repeat the pptn. of MnO_2 in the filtrate. Dissolve the combined ppt. on the filter in HCl (1:1) and H_2O_2, evaporate the soln. to dryness with 5 ml of 20 to 25% H_2SO_4, dissolve the residue in 5 ml of 20 to 25% H_2SO_4, and to the cold soln. add 5 ml of NH_4I soln. (10 mg of iodine per ml) and then 10 ml of 1·5% methyl violet (**I**) soln. in 5% HCl. Wash the ppt., containing Sb and oxidation products of **I**, with a soln. of **I** (25 ml of conc. H_2SO_4 and 10 ml of 1·5% **I** soln. in 500 ml of water), ash it, and ignite at 500° to 600°. Dissolve the residue in hot 20 to 25% H_2SO_4 and filter. To the resulting soln. (3 to 5 ml) add 5 ml of NH_4I - ascorbic acid soln. (12 g and 1 g, respectively, in 100 ml of water), dilute the resulting yellow soln. with 20 to 25% H_2SO_4 to 15 or 20 ml and measure the extinction with a blue filter. Statistical treatment of the results of 5 determinations on alloy M2, containing ≥ 0·005% of Sb, gave a coeff. of variation of 3·38%. C. D. Kopkin

4077. **Flame-spectrophotometric study of silver.** J. A. Dean and C. B. Stubblefield (Univ. of Tennessee, Knoxville, U.S.A.). *Anal. Chem.*, 1961, **33** (3), 382–386.—The flame-emission characteristics of the lines at 328 and 338·3 mμ of Ag (50 to 200 p.p.m.) volatilised from aq. soln. or from soln. in methanol, isopropyl alcohol or isobutyl methyl ketone are reported and discussed in respect of the optimum ratios of O and H (or acetylene) and of their flow rates, the effect of varying burner-heights and background emission. The spectral and radiation interferences of anions and metals other than Ag likely to be present are summarised. No optimum conditions for the determination of Ag (100 to 2000 p.p.m.) are established; favourable results (reproducibility 3%) are obtained with the 328-mμ line, a 0·03-mm slit, and flow rates of 4·7 and 13·5 cu. ft. per hr. for O and H, respectively, or 5·5 and 5·0 cu. ft. per hr. for O and acetylene, respectively. W. J. Baker

4078. **Spectrophotometric determination of trace amounts of silver by toluene-3,4-dithiol.** J. P. Dux and W. R. Feairheller (American Viscose Corp., Marcus Hook, Pa., U.S.A.). *Anal. Chem.*, 1961, **33** (3), 445–447.—The method consists in measuring the extinction (at 416 mμ and after 1 hr.) of a dispersion of the Ag - toluene-3,4-dithiol complex in aq. H_2SO_4, formed with the aid of 30% Na dodecyl sulphate. Beer's law is not closely followed, so that a calibration curve must be prepared for the range of 4 to 40 μg of Ag per ml, at which concn. the precision is ± 5 to 6%. Lead, Hg, As and Sn must be removed initially. The method is particularly suitable for determining Ag in organic material after wet-ashing. W. J. Baker

4079. ***p*-Anisidine reaction for tervalent gold ion.** A. N. Chechneva. *Trudy Ural'sk. Politekh. Inst.*, 1960, (96), 134–137; *Ref. Zhur., Khim.*, 1961, (4), Abstr. No. 4D42.—A new colour reaction between Au^{3+} and *p*-anisidine is the basis for the detection of Au (10^{-6} g per ml). The reaction is used for the detection of Au in electrolytic sludge and can be carried out in 2 to 5 min. K. R. Cook

4080. **A critical examination of the gravimetric and titrimetric methods for the determination of gold.** F. E. Beamish (Dept. of Chem., Univ. of Toronto, Ont., Canada). *Talanta*, 1961, **8** (2–3), 85–103 (in English).—A critical review is presented of methods published before July, 1960. R. M. Rowley

4081. **The analysis of beryllium and beryllium oxide. V. Determination of cadmium.** J. O. Hibbits, S. Kallmann, H. Oberthin and J. Oberthin (General Electric Co., Cincinnati 15, Ohio, U.S.A.). *Talanta*, 1961, **8** (2–3), 104–108 (in English).—Cadmium is co-pptd. with Ni from ammoniacal citrate soln. (pH 8·0 to 8·5) by benzotriazole, the ppt. is digested with HNO_3 and $HClO_4$, and the soln. is evaporated to dryness. The residue is then re-dissolved in 1·2M-HCl. Zinc, Cu and Co are also pptd. by benzotriazole, but Cd and Zn are retained by the resin when the soln. in HCl is passed through Dowex-1 resin, and can then be eluted

with 3M-HNO_3. Cadmium is extracted by dithizone in $CHCl_3$ from strongly alkaline soln. containing hydroxyammonium chloride, tartrate and KCN, and the extinction of the extract is measured at 518 mμ. If more than 100 μg of Zn is present it must be separated by extracting the $CHCl_3$ soln. of the dithizonates with 6M-H_2SO_4, when the Cd will pass into the aq. layer. Up to 10 mg of 66 other elements does not interfere. The method can be used for the determination of 0·5 to 100 μg of Cd in beryllium or its oxide, with an error of ± 3%, or ± 0·3 μg, whichever is the greater.

R. M. ROWLEY

4082. **Spectrophotometric study of the beryllium - thoron complex and its application to the determination of beryllium in alloys.** V. T. Athavale, C. S. Padmanabha Iyer, M. M. Tillu and G. M. Vaidya (Atomic Energy Estab. Trombay, Bombay, India). *Anal. Chim. Acta*, 1961, **24** (3), 263–269 (in English).—The determination of Be in copper, zinc, aluminium and ferrous alloys is described; HNO_3, HCl or H_2SO_4 may be used to dissolve the sample. *Procedure*—To a 10-ml aliquot (1 to 100 μg of Be) add 5 ml of 10% aq. EDTA (disodium salt) soln., and aq. NH_3 to give a pH of 4 to 5. Add 1 ml of 15% (v/v) aq. acetylacetone soln. and conc. aq. NH_3 to give a pH of 7 to 8. After 5 min., extract with CCl_4 (4 × 5 ml) for 7 min., adding 1 ml of acetylacetone soln. before each extraction. Shake the combined organic layers for 7 min. with HCl (3 ml of conc. HCl diluted to 7 ml with water), evaporate the aq. phase to dryness and fume with $HClO_4$. To an aq. soln. of the residue add 2 ml (for 1 to 10 μg of Be) or 10 ml (for 20 to 100 μg) of 0·1% aq. thoron soln. and dilute to 25 (or 100) ml with borate - NaOH buffer (pH 12). Measure the extinction at 470 mμ against a reagent blank.

P. D. PARR-RICHARD

4083. **Quantitative determination of gadolinium in metallic beryllium by the luminescence method.** E. Ya. Arapova, E. G. Baranova, V. L. Levshin, T. V. Timofeeva, A. K. Trofimov and P. P. Feofilov. *Trudy Komiss. Anal. Khim., Akad. Nauk SSSR*, 1960, **12**, 344–354; *Ref. Zhur., Khim.*, 1961, (1), Abstr. No. 1D86.—*Procedure*—Dissolve the sample (5 g) in hot HNO_3 (1:1) with periodic additions of small amounts of H_2O_2. To the cold $Be(NO_3)_2$ soln. add LiCl soln. as flux and Na_2SO_4 soln. to reduce the sinterability of the phosphors (3% of each salt with respect to BeO) and add $Th(NO_3)_4$ soln. to give 1% of ThO_2 with respect to BeO. This addition increases the sensitivity of the phosphors to Gd to 10^{-6} %. Place equal portions of the thoroughly mixed soln. in each of 10 porcelain crucibles, and to 7 of these add various amounts of Gd as $Gd(NO_3)_3$ soln. Evaporate the contents of the crucibles, heat carefully till no more NO_2 is evolved, and ignite the residues at 1000° for 30 min. At high temp. the Gd ions diffuse completely into the ThO_2, leading to the formation of the new phosphor ThO_2.Gd. Carefully grind the prepared phosphors, pack them into cassettes with quartz windows, and excite the luminescence in a spark phosphoroscope (Brumberg *et al., Izv. Akad. Nauk SSSR, Ser. Fiz.*, 1949, **13**, 242). Photograph the luminescence spectra in a quartz spectrograph (aperture ratio 1:3·5) with an exposure of 3 to 5 min., or in a high-transmission apparatus with a quartz optical system and a filter of max. transmission 313 mμ, with an exposure of 30 to 60 sec. Use the doublet 3133 A - 3125 A as analytical line. Construct a calibration curve and extrapolate it to intersect with the abscissa to give the initial concn. of Gd. The use of the method of small additions allows the influence of other admixtures to be ignored, since the degree of weakening of the intensity of the Gd analytical line is independent of the concn. of activator in the phosphor. The mean error is 30 to 50% at a Gd concn. of $\simeq 10^{-5}$ %. Detailed characteristics of the phosphor used are given.

C. D. KOPKIN

4084. **Apparatus for the rapid determination of calcium sulphate in plasters or in mixtures of calcium sulphate and calcium carbonate with the aid of cation exchanger KPS 200.** H. Kniestedt and J. Wahle (VEB Leuna Werke "Walter Ulbricht"). *Chem. Tech., Berlin*, 1961, **13** (2), 110.—The Pièce method (*Schweiz. Arch. angew. Wiss.*, 1959, **25**, 221), based on the adsorption of the Ca^{2+} on cation-exchange resin Amberlite IR-120, and titration of the separated SO_4^{2-} as H_2SO_4, is improved (greatly reduced operating time, better separation of Ca^{2+} and SO_4^{2-}, and simplified apparatus) by using Wofatit KPS 200 as the ion-exchange resin. With mixtures of $CaSO_4$ and $CaCO_3$ all the Ca^{2+} is retained by the resin. *Procedure*—The neutral moist resin (50 g) is stirred for 30 min. with 0·2 to 0·3 g of the finely powdered sample (particle size < 0·06 mm) and 300 ml of water at 90°; after filtration, the filtrate plus washings are titrated with 0·1N-NaOH, to methyl red. If Cl^- are present in the sample in appreciable amount, a correction must be made. If subsequent complexometric determinations of the separated Ca (and Mg and Fe) are to be made in an analysis of a plaster, the complete analysis takes only 2 days as against the 4 days necessary when using Amberlite (*loc. cit.*) for the separation.

H. L. WHITEHEAD

4085. **Rapid method for determining barium in glass.** E. Minchevski, Ya. Frȳdel' and Z. Marchenko (Warsaw Technol. Inst.). *Zavod. Lab.*, 1961, **27** (3), 277–279.—The soln. obtained after removal of the sesquihydroxides is titrated with EDTA (disodium salt) for the total of Ba, Ca and Mg. In another portion Ba is pptd. as $BaSO_4$ and the Ca and Mg are titrated in the presence of the ppt. The difference in the titrations gives the content of Ba.

G. S. SMITH

4086. **Method for determining barium-140 and lanthanum-140 in a mixture of the two radioisotopes.** W. B. Lane (U.S. Naval Radiological Defense Lab., San Francisco 24, Calif., U.S.A.). *Anal. Chem.*, 1961, **33** (3), 478.—In the method described, a scintillation counter with a NaI crystal and a 4-π ionisation chamber are used. The over-all accuracy is better than 10%.

C. B. BAINES

4087. **Photometric determination of small amounts of zinc in bearing metal. II.** N. V. Kostin and A. S. Pashinkin (School of Anal. Chem., Moscow Univ.). *Vestn. Moskov. Univ., Ser. Khim.*, 1961, (1), 64–66.—The method previously described (Kostin, *Anal. Abstr.*, 1960, **7**, 4147) has been verified by adding ^{65}Zn to synthetic alloys and measuring the γ-activity at various stages in the procedure. It was found that Zn is not co-pptd. with $PbCl_2$ and that it is quant. extracted by dithizone at pH 6.

J. W. PRICE

4088. **Spectrographic determination of impurities in high-purity zinc.** N. A. Porkhunova and N. S. Bakaldina. "Spektr. Anal. v Tsvet. Metall.", M.,

Metallurgizdat, 1960, 167–171; *Ref. Zhur., Khim.*, 1961, (1), Abstr. No. 1D153.—Place the sample, finely ground and sieved through a screen (0·5-mm mesh), in a cavity of diam. 4 mm and depth 6 mm in a carbon electrode and excite the spectrum in an a.c. arc at 10 amp. for 80 sec. for the determination of Cu, Pb and Sn, substituting a fresh lower electrode for the determination of Cd. The arc-gap formed by the upper carbon electrode, shaped to a blunt cone, is 3·5 mm. For the first 10 sec. of the exposure use a current of 4 amp. Photograph the spectra in a medium quartz spectrograph. The background is used instead of a comparison line. The analysis is made by the one-standard method, assuming that the calibration curve has a slope of unity. The analytical lines (A) and sensitivities (%) are—Cu, 3247·5, 10^{-4}; Pb, 2833·0, 5×10^{-5}; Sn, 3175·0, 5×10^{-4}; and Cd, 2288·0, 3×10^{-5}. The error is 25 to 30%. The results agree satisfactorily with those by the polarographic method. In the discussion, doubt is thrown on the possibility of correct determinations by the one-standard method, because of the high probability of introducing contamination during the analysis. C. D. KOPKIN

4089. **Determination of small amounts of mercury(II) in the presence of organically combined mercury.** G. Kedvessy. *Pharm. Zentralh.*, 1961, **100** (3), 109–111.—Mix the aq. soln. (9 ml, containing 10 to 80 μg of Hg^{2+} per ml) with a fresh satd. soln. of sym.-diphenylcarbazide in 96% ethanol (1 ml), set aside for 5 min. and measure the violet colour in a Pulfrich photometer with a S57 filter and a 0·5-cm cell. The pH of the soln. should be within the range 3 to 4. The presence of Cl^- causes low results. A. R. ROGERS

4090. **Polarimetric determination of boron.** D. D. DeFord, A. S. Blonder and R. S. Braman (Dept. of Chem., Northwestern Univ., Evanstown, Ill., U.S.A.). *Anal. Chem.*, 1961, **33** (3), 471–472.—The method, applicable to the determination of (*a*) total B (as H_3BO_3 or borates) in the presence of F^- and PO_4^{3-} or (*b*) borate in borohydrides, is based on the high sp. rotation (+ 22°) of the mannitol - borate complex. *Procedure* (*a*)—To the sample add 25 ml of a 10% soln. of mannitol in 1·6M-aq. NH_3 - 2M-NH_4Cl, dilute to 50 ml and, after mixing, measure the rotation. *Procedure* (*b*)—To $\simeq$ 3 g of sample add 25 ml of a 10% soln. of mannitol in 0·6M-NaOH, dilute to 50 ml and measure the rotation within 10 min. after mixing. In both instances the wt. of B_2O_3 is calculated from the respective calibration curves. Control of variables for highest accuracy is discussed. The method is more generally applicable and less subject to interferences than is the polarimetric method of Rosenheim and Leyser (*Z. anorg. Chem.*, 1921, **119**, 1) although the sensitivity is only about one-fifth that of the latter method. W. J. BAKER

4091. **Quantitative spectroscopic analysis of the isotopic composition of boron.** R. V. L'vov and E. M. Mosichev. *Atomnaya Energiya*, 1961, **10** (3), 279–281.—The isotope shift in the emission spectrum of the molecule BO is large enough to be resolved by the usual quartz spectrograph. Intensity ratios of the bands ^{11}BO at 2460·59 A and ^{10}BO at 2460·81 A showed good agreement with the ratios of isotope concn. obtained with a mass spectrograph. Divergent results were obtained at high concn. of the ^{10}B isotope owing to difficulties in determining the background. J. W. PRICE

4092. **Spectrographic determination of boron in water-free borates.** M. M. Kosheleva and T. I. Kuznetsova (Ya. V. Samollov Sci. Inst. for Fertilisers and Insectofungicides). *Zavod. Lab.*, 1961, **27** (3), 312–313.—Variations in the intensity of lines of B at the same concn. in different materials of similar type are eliminated by the use of red phosphorus. G. S. SMITH

4093. **Study of the poly(vinyl alcohol) - borate - iodine complex. II. Test papers [for boric acid].** A. J. Monte-Bovi and J. J. Sciarra (Dept. of Pharm. Chem., St. John's Univ., Coll. of Pharm., Jamaica 32, N.Y.). *J. Pharm. Sci.*, 1961, **50** (3), 198–200.—To prepare the test paper, dip porous filter-paper (Whatman No. 3MM or Whatman No. 40) into a 1:1 mixture of 0·1% iodine and 10% poly(vinyl alcohol) (Elvanol 51–05 or Vinol PA–20) soln. and allow to dry in the air. The paper gives a distinct blue colour when treated with a 2% soln. of boric acid (one drop). The test is reliable, accurate and rapid in comparison with the use of turmeric paper. Starch, if present, may give a blue - black colour with the iodine in the test paper, and it should first be rendered inactive by digestion with pancreatin. Additional test papers, treated with poly(vinyl alcohol) - boric acid (to detect iodine) and boric acid - iodine [to detect poly(vinyl alcohol)] have also been developed. A. R. ROGERS

4094. **Determination of decaborane and pentaborane by means of triphenyltetrazolium chloride.** W. H. Hill, L. J. Kuhns, J. M. Merrill, B. J. Palm, J. Seals and U. Urquiza (Univ. of Pittsburgh, Pa., U.S.A.). *Amer. Ind. Hyg. Ass. J.*, 1960, **21**, 231–238.—Triphenyltetrazolium chloride is reduced by diborane, pentaborane or decaborane (and many other reducing agents) in pyridine to the H_2O-insol. formazan. The red colour that develops in solvents such as xylene can be used as a basis of a quant. colorimetric method. Commercial instruments for monitoring industrial atmospheres for borane by this method are available. CHEM. ABSTR.

4095. **Rapid separation and complexometric determination of aluminium.** L. Burglen and P. Longuet (Centre d'Ét. et de Recherches de l'Ind. des Liants Hydrauliques, Paris, France). *Rev. Matér. Constr., C*, 1960, 327–331.—The method is applicable to the soln., after removal of SiO_2, from the acid decomposition of cement, marl, clay or ironstone, especially when high concn. of Fe are present. The Al is converted into sol. aluminate by the addition at $\simeq$ 100° of an excess of 5N-NaOH and Na_2CO_3, which also precipitates Fe, Ti, Mn, Mg and Ca as hydroxides and carbonates (any PO_4^{3-} are pptd. as iron or calcium phosphate). The Al in the slightly acid filtrate is then determined volumetrically by adding an excess of a standard soln. of EDTA (disodium salt) at 25°, and back-titrating the excess at $\simeq$ 100° with a standard soln. of Al^{3+}, haematoxylin being used as internal indicator, in the presence of ammonium acetate - acetic acid buffer. The accuracy is high provided that an excess of K^+ and Ca^{2+} is present in the sample aliquot, which should contain $>$ 1 mg of Al per ml. W. J. BAKER

96. **Method for the complexometric determination of aluminium.** O. Budevski and L. Simova-Filippova. *Compt. Rend. Acad. Bulg. Sci.*, 1961, **14** (3), 179–182 (in German).—Tervalent Al is not directly titratable with EDTA (**I**), because of the slow reaction rate, and the procedure in which the Al^{3+} are boiled with excess of **I** and the excess is back-titrated with standard Pb^{2+} soln. is not specific. In the present method, after titrating the excess of **I** with Pb^{2+} soln., NaF is added to liberate **I** equivalent to the Al^{3+}, followed by titration with Pb^{2+} soln. *Procedure*—Boil the weakly acid test soln. (150 to 200 ml, containing 10 to 50 mg of Al_2O_3) with 20 to 40 ml of 0·05M-**I** for 3 to 4 min. Add methylthymol blue indicator soln. and aq. NH_3 (1:5) to a yellow-grey colour. Add 5 ml of ammonium acetate buffer soln. (95 ml of glacial acetic acid and 115 ml of conc. aq. NH_3 made up to 1 litre), boil for 2 to 3 min., cool and titrate with 0·05M-$Pb(NO_3)_2$ to a violet end-point. Add saturated NaF soln. (20 ml), boil for 2 to 3 min., add more indicator if required, and again titrate with 0·05M-$Pb(NO_3)_2$ (1 ml ≡ 2·548 mg of Al_2O_3). Interferences, and means of overcoming them, are given. Results for 5 certificated mineral samples are tabulated. G. Russell

4097. **Spectrophotometric determination of aluminium with stilbazo.** C. U. Wetlesen and S. H. Omang (Centr. Inst. for Ind. Res., Oslo, Norway). *Anal. Chim. Acta*, 1961, **24** (3), 294–297 (in English).—Stilbazo was found to form a 1:1 complex with Al. The influence of pH, time, temp., and reagent and buffer concn. was studied; under suitable conditions, Beer's law is followed for 0·1 to 0·8 p.p.m. of Al. Complex-forming anions interfered, as did Cu, Sn^{2+}, Mo^{6+}, W^{6+}, Ti^{4+}, V^{4+}, V^{5+}, Fe^{2+}, Fe^{3+} and Cr^{3+}. Small amounts (⩾ 30 p.p.m.) of Sn^{4+}, Ni, Zn, Pb and Cd, and larger amounts (⩾ 300 p.p.m.) of Co, Ca, Mg and Mn^{2+} could be tolerated. P. D. Parr-Richard

4098. **Determination of aluminium by the fluorescence method.** E. A. Bozhevol'nov and V. M. Yanishevskaya. *Zhur. Vses. Khim. Obshch. im. D. I. Mendeleeva*, 1960, **5** (3), 356–357; *Ref. Zhur., Khim.*, 1961, (1), Abstr. No. 1D79.—A method has been developed for determining Al (10^{-5} to 10^{-5} %) in hydrochloric, hydrofluoric, sulphuric and nitric acids, hydrogen peroxide and Na acetate, based on measurement of the intensity of fluorescence of the internally complexed compound of Al with *o*-salicylideneaminophenol. The optimum pH is 5·6 to 6·2; the reagent is added as a 0·01% soln. in acetone (0·15 ml for 5 ml of test soln.). The intensity of fluorescence is measured with monochromator UM-2, equipped with photomultiplier FEU-19 M, and is proportional to the concn. of Al up to 0·5 μg in 5 ml. The acetate buffer soln. used is first purified from Al by passage through a column (diam. 1·0 to 1·2 cm, height 40 to 50 cm) of the anionite EDE-10, with 5-chloro-2,2′,4′-trihydroxyazobenzene-3-sulphonic acid to complex Al; the Al content of the buffer soln. after purification is reduced to 5×10^{-8} %. The sensitivity of the reaction is 0·0025 μg of Al in 5 ml. In the presence of Cu and Fe, which quench the fluorescence due to Al, the method of additions is used, by which Al can be determined without preliminary removal of Cu and Fe. The determination of Al in the acids and hydrogen peroxide is carried out after evaporation in a special apparatus. The error of the determination is ⩾ 20%. C. D. Kopkin

4099. **Direct determination of small amounts of aluminium in siliceous materials by extraction.** F. Vláčil and V. Zátka (Dept. Anal. Chem., Inst. Chem. Technol., Prague). *Chem. Průmysl*, 1961, **11** (3), 139.—*Procedure*—Decompose the finely powdered sample (0·2 g) in a platinum crucible with a mixture of H_2SO_4 (1:3) (1 ml) and HF (5 ml). Then evaporate to fumes, repeat the evaporation with HF (2·5 ml) and evaporate twice with a few ml of H_2O. Fuse the residue with $K_2S_2O_7$ (1·5 g), dissolve the melt in H_2SO_4 (1:9), add conc. H_2SO_4 (2 ml) and dilute with H_2O to 100 ml. To a 10-ml aliquot add cupferron soln. (6%) (0·25 to 0·5 ml) and extract with 5-ml portions of $CHCl_3$ till the extract becomes colourless. To the aq. layer add aq. NH_3 (1:1) (1·5 ml) and 15% Na acetate soln. (pH 5 to 5·6) (20 ml) to which Na_2SO_3 (0·2 g) has been added. Extract with $CHCl_3$ (5 ml) (for the separation of Fe and Ti) and then extract Al from the aq. layer with 8-hydroxyquinoline soln. (1% in $CHCl_3$) (3 × 5 ml). Dry the extract with Na_2SO_4, dilute to 50 ml and measure the extinction at 386 mμ. The method was tested on samples containing 20 to 160 μg of Al in the presence of 150 μg of Ti. The mean error was 4%. J. Zýka

4100. **Determination of hydrogen in solid aluminium and aluminium alloys.** V. A. Danilkin, K. M. Konstantinov and G. I. Bulatova. *Zavod. Lab.*, 1961, **27** (3), 259–261.—The solid sample is heated at 500° to 600° at 10^{-4} torr and the H in the extracted gas is allowed to diffuse through palladium. The content of H is found from the difference in pressure before and after the diffusion. G. S. Smith

4101. **Colour reaction of gallium with methylene blue.** V. K. Kuznetsova and V. S. Yuminov. *Trudy Ural'sk. Politekh. Inst.*, 1960, **96**, 109–112; *Ref. Zhur., Khim.*, 1961, (4), Abstr. No. 4D55.—The determination is based on the reaction of $GaCl_4^-$ with methylene blue (**I**); a compound is formed containing Ga and **I** in the ratio of 1:1; Al, Zn, In, Cd, Cu^{2+}, Ti^{4+}, Pb, Sn^{4+}, As, Mn^{2+}, Cr^{3+}, Co, Ni, V^{5+}, Mg, Bi, Sb^{3+}, Zr, alkali and alkaline-earth metals do not interfere. The interference of Fe^{3+} is suppressed by reduction to Fe^{2+} with ascorbic acid; powerful reducing and oxidising agents interfere. *Procedure*—Add 0·5% **I** soln. in 6N-HCl (0·5 ml), acetone (0·5 ml) and benzene (2 ml) to the test soln. (1 to 2 ml). The appearance of a blue colour in the benzene layer indicates the presence of Ga. The sensitivity of the reaction (visual) is 5×10^{-5} g of Ga per ml of benzene. The method is suitable for the detection of Ga in aluminium. K. R. Cook

4102. **Investigation of the behaviour of gallium halides in halogen acid solutions by ion exchange.** I. P. Alimarin, E. P. Tsintsevich and É. P. Usova (School Anal. Chem., Moscow Univ.). *Vestn. Moskov. Univ., Ser. Khim.*, 1961, (2), 31–35.—It was established that Ga is present in chloride soln. as a negatively charged ion which is not adsorbed on a cation-exchange resin, and this can be used for the separation of Ga from Al. A soln. containing 0·5 mg of Ga and 530 mg of Al in 2N-NaCl was passed through a column of KU-2 resin (Na^+ form); Ga in the percolate was determined photometrically with gallion and Al was eluted from the column with 2N-HCl and determined with 8-hydroxyquinoline. J. W. Price

4103. Determination of indium on an a.c. polarograph. R. G. Pats and S. B. Tsfasman (State Sci. Res. Inst. of Non-Ferrous Metals). *Zavod. Lab.*, 1961, **27** (3), 266–271.—The determination of In ($< 10^{-7}$ mole) in materials containing Cd, Pb, Te, Se, Sb and Sn and large amounts of Fe is studied. With ratios of Fe to In $> 30{,}000:1$, the sample (0·1 to 1 g), *e.g.*, of lead ore or concentrate, is decomposed by HCl and HNO_3 (in the presence of NH_4F if the content of SiO_2 is high), Pb is separated as $PbSO_4$ after evaporation with H_2SO_4, and In and Fe are pptd. by aq. NH_3. The hydroxides are collected and washed, re-dissolved and re-pptd., and then dissolved in the minimum amount of HCl (1:1). The soln. is evaporated almost to dryness and the residue is moistened with conc. HBr and 2 or 3 drops of Br. After evaporation almost to dryness, the residue is dissolved in 13 ml of HBr (1:3) and the soln. is treated with 10 ml of H_3PO_4 (1:3) and diluted to 25 ml. After removal of O, the square-wave polarogram for In ($E_{\frac{1}{2}} = -0{\cdot}42$ V) is obtained on a Mervyn square-wave polarograph. With ratios of Fe to In $>30{,}000:1$, the sample is treated as described above until the hydroxides have been re-pptd. They are then washed with hot 5% NH_4Cl soln. containing some aq. NH_3 and dissolved in 8 ml of HCl (1:3). The soln. is treated with 15 ml of H_3PO_4 (1:3) and diluted to 25 ml. Part of the soln. is then treated with reduced iron and filtered after cessation of bubbling. This operation reduces the Fe in the soln. to Fe^{2+}, in which form it does not interfere in the polarographic reduction of In in HCl - H_3PO_4 soln. The H_3PO_4 is necessary in this case to reduce the interfering action of Sn. With slags and tin ores, the sample is fused with Na_2O_2 in a nickel crucible, the melt is extracted with water, and the insol. matter is washed with 2% NaOH soln. and dissolved in HCl (1:1). The hydroxides of In and Fe are pptd. from this soln. and the determination is finished as described above. G. S. Smith

4104. Chelatometric methods in rapid applied analysis. V. EDTA titration of thallium in monocrystals [of alkali-metal halides]. M. Kratochvil and J. Blecha (Tesla, Nat. Enterprise, Res. Devel. Estab., Premysleni, Prague, Czechoslovakia). *Chemist Analyst*, 1961, **50** (1), 11–12.—*Procedure*—The sample (0·25 to 1 g, to give $\simeq 0{\cdot}6$ mg of Tl) is dissolved in 1 ml of H_2O, 2 ml of HNO_3 is added and the soln. is evaporated to dryness on a water bath. Two further evaporations are made with 4 ml of aqua regia. The residue is dissolved in 20 ml of H_2O, and 2 ml of an acetate buffer (pH 3·8) and 1 drop of xylenol orange soln. (0·1% in acetate buffer) are added. The Tl^{III} is titrated with 0·001M-EDTA (disodium salt) to a change from violet-blue to clear yellow. The method enables a rapid and accurate determination to be made of the distribution of Tl in monocrystals.

J. H. Waton

4105. The ion-exchange separation of the rare-earth elements of the cerium sub-group. V. P. Khramov. *Trudy Saratov. Inst. Mekh. Sel. Khoz.*, 1959 (1960), (19), 15–26; *Ref. Zhur., Khim.*, 1961, (1), Abstr. No. 1D45.—The previously published method of citrate elution (Dodonov *et al.*, "Redkozemel'nye Elementy", publ. Akad. Nauk SSSR, 1958, p. 121) was used for the separation of a mixture of rare-earth elements freed from the main bulk of Ce by pptn. of the double nitrates. The separation was carried out on three columns of cationite NSK (H^+ form) in series. A 358-cm cationite layer was used for the purification of Nd. The cationite was saturated with 0·005N-nitrate, which was passed through the columns at a rate of 75 ml per hr.; a 0·5% soln. of citric acid, adjusted with aq. NH_3 to pH 3·84, was passed at the same rate for the elution. Under these conditions pure Sm is first eluted, and then pure Nd, which is obtained in $> 70\%$ yield. If the cationite layer is reduced to 265 cm, only 45% of the Nd is eluted. Saturation of the columns with 0·005N soln. of the nitrates takes $\simeq 17$ days; to accelerate the process it is recommended to use 0·05N soln. With a cationite layer of 358 cm the yield of Nd is then reduced to 60·9%. The pH of the initial soln. of nitrates greatly influences the efficiency of the separation; if the pH is reduced to 2 it becomes impossible to obtain pure products. C. D. Kopkin

4106. Determination of carbon, oxygen and silicon in solids by activation analysis, with 15-MeV deuterons. J. W. Winchester and M. L. Bottino (Dept. of Geol. and Geophys., M.I.T., Cambridge 39, Mass., U.S.A.). *Anal. Chem.*, 1961, **33** (3), 472–473.—A method is described for determining small amounts of C in pure silicon dioxide. The results show that it is feasible to determine as little as a few tenths per cent. of C without chemical processing; the ratio of Si to O may also be determined. This technique can be extended to any non-volatile matrix. C. B. Baines

4107. Determination of hydrogen cyanide by gas chromatography. K. G. Woolmington (African Explosives and Chem. Industries Ltd., Northrand, Transvaal, S. Africa). *J. Appl. Chem.*, 1961, **11** (3), 114–120.—Water vapour (18 to 32%) and HCN ($< 10\%$) can be separated from O, N, CH_4 and CO by passing the sample (with H as carrier) at $\simeq 160$ ml per min. and at 100° to 107° through a stainless-steel tube (7 ft. by $\frac{3}{8}$ in.) packed with Chromosorb or acid-washed Celite (30 to 60 mesh) impregnated with 20% (w/w) of polyoxyethylene glycol 1500. The permanent gases emerge first (1 to 2 min.), followed after 3 to 4 min. by HCN, and finally after 8 to 10 min. by water vapour. The concn. of HCN and H_2O can be calculated from the peak heights. If HCN and water vapour are removed from the gas stream by adsorption on silica gel, the permanent gases can be separated on a second, shorter column packed with Linde 5A molecular sieve. If the lengths of the two columns are adjusted so that N emerges from the second column shortly after the emergence of HCN from the first, a simultaneous determination of HCN and N can be made with only one recorder. If water vapour is absent or is removed from the sample, the first column can be operated at a lower temp. The calibration graph for HCN is prepared with dry gas mixtures; values obtained with wet gas mixtures are always $\simeq 0{\cdot}1\%$ high. The accuracy and precision are claimed to be superior to those of the usual chemical methods. W. J. Baker

4108. New method for the polarographic determination of cyanide. J. S. Hetman (Southern Analytical Ltd., Camberley, Surrey, England). *Lab. Practice*, 1961, **10** (3), 155–156.—Cyanide ions are reduced in a basal electrolyte of pyridine and KNO_3 to which Hg^{2+} have been added. The wave height is proportional to concn. over the range 2 to 48 p.p.m. of CN^-. *Procedure*—The test soln. is added to 2 ml of $HgCl_2$ soln. (0·2%), 2 ml of pyridine and 2 ml of gelatin soln. (0·2%), and the mixture is diluted to exactly 20 ml with

N-KNO_3. Aliquots (5 ml) are deoxygenated and polarograms plotted over the range 0 to 0·5 V. Many ions do not interfere, but Cu^{2+} and S^{2-} must be removed. The method is suitable for the determination of CN^- in the presence of excess of methyl cyanide, hydrazine sulphate, azides, NH_3 and *p*-chlorophenylacetonitrile. J. H. WATON

4109. **Application of catechol violet as a colorimetric reagent for tin.** W. J. Ross and J. C. White (Oak Ridge Nat. Lab., Tenn., U.S.A.). *Anal. Chem.*, 1961, **33** (3), 421–424.—Tin can be determined spectrophotometrically at 555 mμ as the red complex of Sn^{4+} with catechol violet (0·05%, w/v, aq. soln.) formed at pH 2·5. Gallium, Zr, Ti, Bi, Sb and Mo interfere by forming similar complexes at pH < 5; SO_4^{2-} and NO_3^- do not interfere if Cl^- are present. Beer's law is followed for concn. of Sn from 0·24 to 1·6 μg per ml, and the molar absorptivity is $6·5 \times 10^4$. Bivalent Sn does not react with the colour reagent. The method, which can be applied after the distillation of Sn as $SnBr_4$, is claimed to be more sensitive and less subject to error than the usual colorimetric methods. W. J. BAKER

4110. **Spectrographic analysis of high-purity tin with preliminary enrichment.** D. M. Shvartz and V. V. Portnova. "Spektr. Anal. v Tsvet. Metall.", M., Metallurgizdat, 1960, 125–136; *Ref. Zhur., Khim.*, 1961, (1), Abstr. No. 1D157.—The method comprises three stages, *viz*, conversion of the metal into $SnCl_4$, removal of the base and concentration of the impurities, and analysis of the concentrate. *Procedure*—Place the finely ground tin (5 g) in a test-tube, add 10 ml of CCl_4 and pass Cl, free from O and moisture, for 3 to 3·5 hr. To the resulting soln. add 0·03 g of activated carbon and set aside for 15 to 16 hr., shaking the tube 2 or 3 times at intervals of 1 to 2 min. Filter off and dry the residue at 40° to 45°. Remove the powder containing the impurities from the filter with a plastic spatula and place it in a cavity of depth 3 mm and diam. 4 mm in the lower carbon electrode. The upper electrode is sharpened to a truncated cone with a flat surface of diam. 2 mm. The electrodes are first ignited by passing a current of ≃ 300 amp. Excite the spectra in an anodic d.c. arc and photograph in a medium quartz spectrograph with three-lens illumination and an intermediate 5-mm diaphragm. Each spectrum is obtained by igniting two samples on carbon, for 2 × 80 sec. Construct calibration curves from the most sensitive lines of the elements Co, Sb, Au, Bi, Pb, Ga, Ni, Ag and In. The determinable concn. are from 5×10^{-7} to 3×10^{-3} %. The mean error is 19 to 25%. C. D. KOPKIN

4111. **Extraction of tin with tri-(2-ethylhexyl)-phosphine oxide and its determination in non-aqueous medium with catechol violet.** W. J. Ross and J. C. White (Oak Ridge Nat. Lab., Tenn., U.S.A.). *Anal. Chem.*, 1961, **33** (3), 424–427.—A specific spectrophotometric method is given for determining Sn in lead, zinc, copper, iron and zirconium alloys. *Procedure*—Adjust an aliquot (10 to 100 μg of Sn) of the sample soln. to 5 ml and to be M in HCl and 2 to 3M in H_2SO_4. Extract this soln. for 10 min. with 5 ml of 0·01M-tri-(2-ethylhexyl)phosphine oxide in cyclohexane; to an aliquot of the organic phase add 0·05% ethanolic catechol violet (2 ml) and pyridine (1 ml), and dilute to 10 ml with 95% ethanol. Shake well, heat the stoppered flask at 55° to 60° for 20 min. and then measure the extinction of the Sn^{4+} complex at 575 mμ against either ethanol or a reagent blank. Although the calibration curve does not conform to Beer's law, it is sufficiently accurate for the determination of 2 to 20 μg of Sn. The coeff. of variation increases from 1 to 5% for contents of Sn decreasing from ≃ 5 to 0·5% (2 to 6 analyses of each alloy). Co-extraction of Ga, Sb, Fe and Mo is remedied by back-washing the initial organic phase with M-HCl - 2M-H_2SO_4. W. J. BAKER

4112. **Precipitation of lead with anion-exchanger sulphates.** M. Ziegler (Anorg.-Chem. Inst., Univ., Göttingen, Germany). *Z. anal. Chem.*, 1961, **180** (1), 1–4 (in German).—*Procedure*—Convert Dowex 1 (20 to 50 mesh) into the SO_4^{2-} form by treating with H_2SO_4 (10%) and washing till neutral. Fill a column (10 cm × 0·8 cm) with the resin and wash with aq. methanol (1:1) (40 ml). Cover the resin layer with 0·5 cm of cotton wool. To the lead soln. (2 to 150 mg of Pb, HNO_3 ≯ 2 ml in 50 ml) add an equal vol. of methanol. Pass this soln. through the column at 2 drops per sec. and wash with aq. methanol (1:1) (10 to 40 ml). Elute the Pb with 3% NaOH soln. (25 ml) and wash the resin with water (30 ml). Determine the Pb either by titration with EDTA or photometrically as sulphide. In the latter case, add to the lead soln. (50 ml) 4% poly(vinyl alcohol) soln. (10 ml) and pass H_2S. Measure the extinction at 370 mμ. The colour is directly proportional to the concn. over the range 0 to 1000 μg of Pb per 50 ml, and is stable for 4 hr. The procedure was successful with the following ratios of Pb to other cations—Fe (1:2); Co (1:35); Ni (1:70); Cu (1:10); Mg (1:500); Ba (1:4) and Sr (1:2). The mean coeff. of variation in 47 determinations was ± 0·7%. G. RUSSELL

4113. **An ion-exchange separation and polarographic determination of small amounts of lead and zinc in the presence of cobalt.** R. Carson (Rhoanglo Mine Services Ltd., Res. and Devel. Div., Kitwe, N. Rhodesia). *Analyst*, 1961, **86**, 198–200.—A column in 1% (v/v) HCl of a strongly basic anion-exchange resin (*e.g.*, De-Acidite FF), graded according to a specified procedure, is washed successively with a wash soln. (10 ml of conc. HCl and 10 ml of satd. SO_2 soln. diluted to 1 litre), 1 litre of water and 300 ml of 2N-HCl. To prepare the standard graphs, 0 to 1-ml portions of standard soln. of Pb and Zn (0·1 mg per ml) are treated with 40 ml of basal electrolyte (250 g of NaCl and 50 ml of 2N-HCl diluted to 1 litre), 5 ml of an ammonium acetate - acetic acid buffer and 0·5 ml of gelatin soln. (1%) and the mixture is diluted to 50 ml. Each soln. in turn is transferred to a polarographic cell containing a static mercury-pool anode, and polarograms are recorded over the ranges − 0·3 to − 0·7 V for Pb and − 1·0 to − 1·45 V for Zn. The graphs are linear. The sample soln. is allowed to percolate through the column and the Ni, Co, Cu, Fe and Mn are eluted with 2N-HCl followed by 0·5N-HCl; Pb and Zn are then eluted with 0·005N-HCl. The fractions of eluate containing Pb and Zn are evaporated, and the residue is dissolved in the basal electrolyte for the polarographic determination. A. O. JONES

4114. **Polarographic determination of lead in activated charcoal.** J. Branžovský and O. Kusák (Ind. Chem. School, Ostrava-Hrušov, Czechoslovakia). *Chem. Průmysl*, 1961, **11** (3), 134–135.—The combustion of the samples in the presence of

$Mg(NO_3)_2$ and ethanol prevents oxidation and reduction reactions during the decomposition. Ammonium acetate is used for the separation of the excess of Fe. *Procedure*—Mix the sample (3 g) in a porcelain crucible with $Mg(NO_3)_2.6H_2O$ (12 g), moisten with ethanol (5 ml), dry at 105°, heat gently and then ignite for 1 hr. Treat the residue with HCl (1:1) (20 ml) and evaporate to dryness on a sand bath. Heat the residue with ammonium acetate soln. (40%) (10 ml) and acetic acid (20%) (10 ml), then dilute with H_2O to 250 ml. To a 20-ml aliquot of the suspension add M-ascorbic acid (5 ml) and gelatin soln. (0·5%) (1 ml); dilute with H_2O to 100 ml, filter, and record the polarographic wave from −0·2 to −0·8 V. Evaluate by the method of standard additions. Samples containing 0·007 to 0·07% of Pb were analysed.

J. ZÝKA

4115. **Photometric determination of titanium in the presence of niobium and tantalum as peroxytitanyl 1,2-diaminocyclohexane-*NNN'N'*-tetraacetate.** E. Lassner, R. Püschel and R. Scharf (Metallwerk Plansee A.-G., Reutte, Tirol, Austria). *Z. anal. Chem.*, 1961, **179** (5), 345–349 (in German).—The formation of a 1:1 complex from Ti and Na 1,2-diaminocyclohexane-*NNN'N'*-tetra-acetate (**I**) is used to give greater specificity to the reaction of Ti with H_2O_2. *Procedure*—Treat the sample soln. (1 to 60 mg of Ti), strongly acid with H_2SO_4, with H_2O_2 (100 vol.) (2 ml), 40% tartaric acid soln. (10 ml), **I** soln. (neutralise 5 g of acid with NaOH, dilute to 100 ml) (5 ml) and 40% Na acetate soln. (10 ml). Adjust the pH to 5 ± 0·1 with aq. NH_3 and heat the soln. at 60° to 80° for 20 min. Cool and dilute to 250 ml. Measure the extinction at 370 mμ in a 2-cm cell. To analyse an oxide mixture, fuse with $K_2S_2O_7$, extract with H_2SO_4 and proceed as described above. The procedure eliminates interference by Nb and Ta; large amounts of alkali salts or SO_4^{2-} do not interfere. Results for 2 to 60 mg of Ti in the presence of various amounts of Nb and Ta gave a mean relative error of ± 1·2%. The mol. extinction coeff. is 826.

G. RUSSELL

4116. **3-Acetyl-4-hydroxycoumarin as a reagent for the gravimetric determination of zirconium and titanium.** A. N. Bhat and B. D. Jain (Dept. of Chem., Univ., Delhi 6, India). *Proc. Indian Acad. Sci., A*, 1961, **53** (3), 147–150.—Zirconium (2 to 100 mg of ZrO_2 as a zirconyl salt) is quant. pptd. from aq. soln. (pH 3·5 to 7·0) by the addition of 5 ml of 1% ethanolic 3-acetyl-4-hydroxycoumarin soln. The reagent must be added slowly, with constant stirring, and the ppt. allowed to settle for 10 min. in the cold. After filtration and washing with cold water, the ppt. is ignited to ZrO_2. Titanium (7 to 70 mg of TiO_2 as a titanyl salt) may also be determined at pH between 7·0 and 9·0. The reagent (10 ml) is added slowly with stirring, and the soln. is warmed on a water bath for 15 min. When cool the soln. is filtered and the ppt. is washed with water and ignited to TiO_2.

J. H. WATON

4117. **Direct amperometric titration of zirconium with EDTA (disodium salt) with the rotating tantalum micro-electrode.** V. A. Khadeev and F. F. Kvashina. *Izv. Výssh. Ucheb. Zavedenií, Khim. i Khim. Tekhnol.*, 1960, **3** (2), 251–257; *Ref. Zhur., Khim.*, 1961, (1), Abstr. No. 1D93.—A method has been developed for the direct amperometric titration of Zr with EDTA (disodium salt) in a basal soln. of H_2SO_4, HNO_3 or HCl (acid concn. ≯ N) by means of the oxidation current of EDTA (disodium salt) on the rotating tantalum micro-electrode at + 1·2 V *vs.* the S.C.E. Small or large amounts of Zr can be determined with high accuracy. Large amounts of Cl^-, NO_3^-, acetate, BO_3^{3-}, Be, Zn, Co, U, Th, Cd, Mo and Pb, and 10-fold amounts of Cr, Ni, Ce^{3+}, V^V, hydrazine sulphate or hydroxyammonium chloride do not interfere; serious interference is caused by CrO_4^{2-}, Fe^{3+}, Sb, Bi, Sn^{4+}, Ta, W and Mn, and considerable interference by F^-, Hg and Cu; the interference of the last three is reduced in the presence of Al^{3+}, Cl^- and tartaric acid, respectively. After 10 to 15 titrations the tantalum electrode should be ignited in an alcohol flame.

C. D. KOPKIN

4118. **Determination of combined nitrogen in zirconium and Zircaloy.** C. F. Bush [U.K.A.E.A. (Res. Group), Chem. Div., Chatham Outstation, Kent, England]. Analytical Method AERE–AM78, 1961. 8 pp.—The sample is dissolved in 5% HF in a platinum dish, with the addition (if necessary) of H_2O_2 and/or H_2SO_4 for Zircaloy. After a Kjeldahl distillation, the NH_3 is determined absorptiometrically with Nessler reagent. Except at the lowest levels, the max. error for amounts of N up to 300 μg is ± 5%.

W. J. BAKER

4119. **Spectrographic determination of boron in zirconium.** I. M. Blokh and A. K. Rusanov. *Trudy Komiss. Anal. Khim., Akad. Nauk SSSR*, 1960, **12**, 160–165; *Ref. Zhur., Khim.*, 1961, (1), Abstr. No. 1D121.—A method is developed for determining B in zirconium used in reactor construction. *Procedure*—Convert the Zr into oxide by heating in a muffle-furnace. Add 1% of Ga (as Ga_2O_3) as carrier, and place 70 mg of the mixture in a cavity of depth 8 mm and diam. 4 mm in the lower boron-free graphite electrode. The counter-electrode is sharpened to a cone. Excite the spectra in a d.c. arc at 10 amp. Construct calibration curves for each plate from synthetic standards over the concn. range 5×10^{-6} to 10^{-3} %. The ZrO_2 used for standards is prepared from Zr purified from B via the oxychloride. The standards are prepared by adding borax. The reproducibility is within 12%. A preliminary enrichment by distillation of B *in vacuo* increases the sensitivity, but the error increases to 20%.

C. D. KOPKIN

4120. **Polarographic determination of nitrite and nitrate.** R. Annino and J. E. McDonald (Dept. of Chem., Northeast Louisiana State College, Monroe, U.S.A.). *Anal. Chem.*, 1961, **33** (3), 475.—By the method described, a complete analysis of both nitrite and nitrate can be achieved in 30 min. Nitrite is determined at − 1·2 V *vs.* the S.C.E., with citric acid - Na citrate buffer (pH 2·0) as the basal electrolyte, and concn. of nitrite in the presence of 100 times as much nitrate on a molar basis can be easily measured with an accuracy and precision of 1 to 2% relative. Nitrate is determined at −1·2 V *vs.* the S.C.E., in a basal electrolyte containing UO_2^{2+}, after the nitrite has been removed with hydrazoic acid.

C. B. BAINES

4121. **Flame-photometric determination of phosphorus in the presence of sodium, potassium and other cations.** D. N. Bernhart, W. B. Chess and D. Roy (Victor Chemical Works, Stauffer Chemical Co., Chicago Heights, Ill., U.S.A.). *Anal. Chem.*, 1961, **33** (3), 395–396.—The sample (= 0·5 to 0·6 g of P_2O_5) is dissolved in 120 ml of HCl

(1:7), the soln. is diluted to 250 ml with H_2O, and the P is then determined directly, in a 25-ml aliquot, by its interference with the 100% flame-emission of Sr at 660 mμ. The $SrCl_2$ soln. is added to the aliquot so that the final soln. (100 ml) contains 1·2 mg of Sr per ml. For the lower oxidation states of P, special calibration curves are required because the interference decreases. The results are satisfactory for the orthophosphates of K, NH_4^+, Mg and Cu, and for the ortho-, cyclic and condensed phosphates of Na. The standard deviation was 0·30% for 25 analyses of sodium tripolyphosphate (**I**) (57·5% of P_2O_5), but was 0·12% (3 readings) when the calibration curve was prepared with **I**. W. J. BAKER

4122. **Volumetric analysis of phosphates.** D. C. Cullum and D. B. Thomas (Colgate-Palmolive Ltd., Salford, Lancs., England). *Anal. Chim. Acta*, 1961, **24** (3), 205–213 (in English).—Phosphates in detergent powders are converted into the MH_2PO_4 form, and determined by pptn. with $AgNO_3$ and potentiometric titration of the liberated acid; BO_3^{3-}, CO_3^{2-}, SiO_3^{2-} and SO_4^{2-} do not interfere, and BO_2^- can be determined subsequently. Sulphonate should be absent. *Procedure*—To a sample containing 0·1 g of P_2O_5 in ≃ 100 ml of H_2O add 3N-HNO_3, with stirring, until the pH is < 4·5, and adjust finally to 4·5 to 4·6 with 0·1N-NaOH. Add 1 ml of 20% NH_4NO_3 soln. and a 3-fold excess of 10% $AgNO_3$ soln. Titrate with NaOH soln. to a pH of 4·8 to 4·9. The method can be modified to determine the chain lengths of condensed phosphates.

P. D. PARR-RICHARD

4123. **Rapid trace analysis of phosphate mixtures by a paper-chromatographic densitometric procedure.** R. H. Kolloff (Monsanto Chemical Co., St. Louis, Mo., U.S.A.). *Anal. Chem.*, 1961, **33** (3), 373–379.—The procedures described are applicable to the determination of $Na_4P_2O_7$ (0·01 to 0·5%) in trisodium and disodium hydrogen orthophosphates, of $Ca_2P_2O_7$ (0·1 to 2%) in calcium hydrogen orthophosphate, and of trace amounts of sol. long-chain phosphates (*A*) in commercial $Na_5P_3O_{10}$ or detergents. High sensitivity and accuracy are attained by using (*i*) Whatman 31 DT chromatographic paper, which scarcely deteriorates after the complete hydrolysis of *A*, and (*ii*) a primary spray of acid ammonium molybdate, followed by an ammoniacal selective reducing spray based on 1-amino-2-naphthol-4-sulphonic acid, which ensures complete absence of background colour. According to the nature of the sample, the solvent is chosen from five standard mixtures of dioxan - trichloroacetic acid - aq. NH_3 - H_2O, and the hydrolysis is effected at 100° for ≃ 30 min. in the apparatus described and illustrated. The chromatogram containing the spots of one phosphate species is scanned in the densitometer at 90° to the direction of solvent flow. The sensitivity and accuracy are less than for the lengthy thiocyanate colorimetric method (Kolloff *et al.*, *Anal. Abstr.*, 1961, **8**, 2368), but interferences (Fe^{3+}, Ca^{2+}, band interaction, variations in content of PO_4^{3-}) are much less troublesome. The components in a sample of *A* can be resolved in a 45-min. unidirectional run. W. J. BAKER

4124. **Spectrophotometric determination of phosphate in the presence of highly labile phosphorus compounds.** L. C. Mokrasch (Dept. of Med., State Univ. Med. Center, Kansas City, U.S.A.). *Anal. Chem.*, 1961, **33** (3), 432–434.—To avoid hydrolysis of labile phosphorus compounds and to increase the sensitivity, the usual molybdate method is modified by mixing the colour reagent (2·5 ml) with the sample (0·5 ml, ≡ > 0·1 μmole of PO_4^{3-}) and after 2 to 10 min. adding 0·06M-ascorbic acid (0·1 ml), followed after a further 2 to 30 min. by measurement of the extinction at 335 mμ. The colour reagent is a mixture of 8·1mM-ammonium molybdate, 0·54M-acetic acid - 0·05M-K acetate - 0·03mM-$CuSO_4$, and dimethylformamide (1:5:20). Protein in high concn. must be removed by centrifugation during the period of colour development. Applications, permissible variations in procedure, and sources of interference are discussed.

W. J. BAKER

4125. **Automation of ion-exchange chromatographic analysis of condensed phosphate mixtures.** D. P. Lundgren and N. P. Loeb (Res. and Devel. Div., Lever Brothers Co., Edgewater, N.J., U.S.A.). *Anal. Chem.*, 1961, **33** (3), 366–370.—A rapid, automatic method, relatively free from interference, is described in which an ion-exchange chromatographic column of AG1-X8 (100 to 200 mesh) (Cl^- form) is coupled with a gradient elution system and connected to an automatic analyser. This instrument is programmed to conduct a quant. acid degradation of condensed phosphates; a portion of the resulting orthophosphate is isolated by dialysis and is then treated with acid ammonium molybdate to form molybdophosphoric acid. This is reduced with hydrazine sulphate and the concn. of the resulting complex is measured colorimetrically and recorded. The speed of the analysis depends on the complexity of the phosphate mixture, but a sample containing only ortho-, pyro- and tri-phosphate can be analysed in 1 hr. A calculation based on a weighted relative-area calculation of the recorded elution curve finishes the assay. C. B. BAINES

4126. **Detection and separation of higher-molecular phosphates in phosphate mixtures.** C. Riess (J. A. Benckiser G.m.b.H., Ludwigshafen-am-Rhein, Germany). *Z. anal. Chem.*, 1961, **179** (5), 358–359 (in German).—Add to the test soln. (50 ml, containing ≃ 100 mg of high-molecular phosphate) 10% acetic acid (10 ml), cool in ice and then add an ice-cold 1% soln. of cinchonine sulphate (50 ml). Filter through a hard paper and wash with acetic acid (1%, containing a little cinchonine sulphate). Dissolve the ppt. in H_2SO_4 and determine the P as $MgNH_4PO_4.6H_2O$. The detection limit for pptn. is ≃ 1 in 2×10^5. Mono-, di- and tri-phosphates and trimetaphosphate give no ppt. even when present in a 100-fold excess, unless Ca or Mg is also present. Soluble silicates do not interfere, but organic sulphonic acids must be absent. In tests on known substances (Graham's salt, Tamman's salt), 90 to 100% of the available P is pptd. Nephelometric measurements may be made on individual phosphates, but the values are not comparable between different phosphates.

G. RUSSELL

4127. **Preparation and methods of determination of hypophosphate.** W. G. Palmer (Univ. Chem. Lab., Cambridge, England). *J. Chem. Soc.*, 1961, 1079–1082.—Four methods are described for the determination of hypophosphate (**I**) in the presence of other phosphorus oxy-anions—(*i*) oxidation by iodic acid at 100° in the presence of 40% H_2SO_4, followed by distillation of iodine and

titration with arsenite; (*ii*) pptn. as $Ag_4P_2O_6$ from a medium containing 0·5M-HNO_3; (*iii*) pptn. as $Zn_2P_2O_6$ at pH 4 followed by conversion of this ppt. into $Ag_4P_2O_6$; (*iv*) oxidation by aq. bromine soln. at pH 7·7 followed by back-titration of the excess of Br. Method (*i*) cannot be used in the presence of other reducing oxy-anions of phosphorus. Method (*ii*) separates **I** completely from ortho-, di- and tri-phosphate and from trimeta-phosphate, but tetrameta- and polymeta-phosphate interfere. The only common phosphorus oxy-anion that interferes with method (*iii*) is pyrophosphate. Method (*iv*) can be used to distinguish hypophosphite and phosphite from **I**; hypophosphite and phosphite are oxidised by Br in strongly acid soln., but **I** is oxidised only in the pH range 6 to 9.

A. R. ROGERS

4128. **Polarographic determination of microgram amounts of arsenic and antimony in silicates.** Yu. V. Morachevskiĭ and A. I. Kalinin (Inst. of Silicate Chemistry, Acad. Sci., USSR). *Zavod. Lab.*, 1961, **27** (3), 272–274.—The sample (1 g) in a platinum dish is decomposed by 15 ml of HF and 1 ml of H_2SO_4 and the soln. is evaporated to fuming. The residue is dissolved in the minimum amount of water and the soln. is treated with 0·5 g of KBr, 20 ml of H_2SO_4, 10 ml of HCl and 0·1 g of hydrazine sulphate. Distillation of the chlorides of As and Sb together is carried out on a glycerol bath and the distillate is received in 10 ml of water. The flask is heated to 80° and a mixture of 10 ml of water containing 0·5 g of KBr and 20 ml of H_2SO_4 is added dropwise. The temperature is then raised and the soln. is maintained at 190° to 200° for 1 hr. The distillate is treated with 2 ml of HNO_3 and evaporated to 1 to 2 ml, and then to fuming with 1 ml of H_2SO_4 (1:5), followed by addition of 0·1 g of hydrazine sulphate (to reduce As^V to As^{III}) and evaporation to dryness. The residue is dissolved in 1 ml of the basal soln. (N-H_2SO_4, 0·5M in KCl and 10^{-5}M in methylene blue), O is removed, and the polarogram for As and Sb is recorded.

G. S. SMITH

4129. **Determination of antimony in technical alloys.** M. E. Gárate and F. Burriel-Martí (Lab. Centr. R.E.N.F.E., Madrid, Spain). *Rev. Univ. Ind. Santander, Colombia*, 1961, **3** (1), 13–16.—The most suitable reagent for dissolving antimony alloys for analysis is a mixture of HNO_3 and HF diluted with H_2O, the optimum proportions varying according to the type of alloy. The Sb goes into soln. as Sb^{3+} and may be determined by potentiometric titration with $KBrO_3$ soln. with a platinum wire - normal calomel electrode pair, without separation of other elements. Only As interferes.

L. A. O'NEILL

4130. **Spectrographic determination of bismuth and copper in a phosphor based on strontium sulphide.** L. A. Dvorzhetskaya and L. Ya. Khlebnikova. *Sb. Trud. Gos. Inst. Prikl. Khim.*, 1960, (43), 161–162; *Ref. Zhur., Khim.*, 1961, (1), Abstr. No. 1D172.—To study possible losses of activators in the firing of the charge, a method is developed for the determination in strontium sulphide of Bi in the range 10^{-3} to 10^{-1} % and of Cu in the range 10^{-4} to 10^{-2} %. *Procedure*—Excite the spectra in a d.c. arc at 10 amp. by evaporation from a cavity in the graphite electrode used as anode. The measurements are made from the intensity of the lines Bi 3068 and 2897A, and Cu 3247 A. Prepare standards synthetically by grinding the powders for 1 hr. in an agate mortar. The error of the determination is 20% for Bi and 15% for Cu.

C. D. KOPKIN

4131. **Analysis of bismuth for impurities.** Sh. G. Melamed and S. M. Solodovnik. *Trudy Komiss. Anal. Khim., Akad. Nauk SSSR*, 1960, **12**, 172–174; *Ref. Zhur., Khim.*, 1961, (1), Abstr. No. 1D164.—For the spectrographic determination of As, Pb and Cu, the electrodes used are rods of metallic bismuth of diam. 9 mm, cast in an iron mould. The spectra are excited in the spark discharge of generator IG-2 by using a complex circuit with the following characteristics—current in primary circuit, 1·2 amp.; capacity, 0·005 μF; self-inductance, 0·55 mH; analytical gap, 2 mm; and secondary gap, 2·5 mm. The spectra are photographed after preliminary ignition for 30 sec. Standards are prepared synthetically with pure bismuth as base. The sensitivity of the determination from the resonance lines is 10^{-3} % for As, 3×10^{-5} % for Cu and 10^{-3} % for Pb. The coeff. of variation is 6%. To determine Sb, to 5 g of metallic bismuth add 20 mg of Sn and treat the mixture in the cold with 45 ml of HNO_3 (sp. gr. 1·4) and then add 120 ml of hot 3% HNO_3. Allow the ppt. to settle, collect it and ignite. Excite the spectra in an arc at 8 amp. by evaporating the sample from a cavity in the carbon electrode used as anode. The exposure is $\simeq$ 90 sec. (till the sample is completely evaporated). The sensitivity of the determination of Sb from the line-pair Sb 2769·9 and Sn 2790·19 A is 10^{-4} %. The coeff. of variation is 10%.

C. D. KOPKIN

4132. **Chemico-spectrographic determination of impurities in bismuth and its compounds.** L. S. Krazh, A. G. Karabash, Sh. I. Peĭzulaev, V. M. Lipatova and V. S. Moleva. *Trudy Komiss. Anal. Khim., Akad. Nauk SSSR*, 1960, **12**, 175–186; *Ref. Zhur., Khim.*, 1961, (1), Abstr. No. 1D165.—*Procedure*—Dissolve 10 g of metallic bismuth in 50 ml of 7N-HNO_3, heat the soln. to remove oxides of N, dilute to $\simeq$ 300 ml with 0·3N-HNO_3 and precipitate Bi at room temp. with freshly prepared HI soln. Remove a measured vol. (275 ml) of the mother liquor by decantation from the pptd. BiI_3 4 hr. after adding the HI, evaporate it in a weighed quartz dish, and ignite the dry residue for 30 min. at 550°. Mix the resulting concentrate (5:1) with spectrographically-pure vitreous BeO. Calculate the enrichment factor of the impurities. Simultaneously with the preparation of the concentrate, prepare a sample, without enrichment, by dissolving 3 to 5 g of sample in 10 to 15 ml of 7N-HNO_3, evaporating to dryness, igniting for 30 min. at 550°, and mixing with BeO. Carry out a blank to allow for possible impurities in the reagents. Prepare standards on Bi_2O_3 as base and dilute with BeO. Excite the spectra in a d.c. carbon arc at 12 amp. An electrode with 120 mg of material in a cavity of diam. 4·5 mm and depth 6 mm is used as the anode. Construct calibration curves allowing for the background. Magnesium, Ca, Ba, Al, Ti, V, Cr, Mo, Mn, Fe, Co, Ni, Zn, Cd, In and Te are determined simultaneously with sensitivity 10^{-4} to 10^{-6} %. Determine Cu, Ag, Au, Sn, Pb, Pt and Tl in the sample without enrichment; these are not completely extracted into the concentrate. The sensitivity of the direct method is 10^{-3} to 10^{-5} %. The error of the analysis is within $\pm$ 20%. Procedures are developed and very briefly described for the determination of Na, Li, B, As and Sm in bismuth.

C. D. KOPKIN

4133. **Determination of lithium in bismuth.** T. F. Borovik-Romanova. *Trudy Komiss. Anal. Khim., Akad. Nauk SSSR*, 1960, **12**, 221–223; *Ref. Zhur., Khim.*, 1961, (1), Abstr. No. 1D57.—*Procedure*—Dissolve the sample (2 g) in HNO_3 (5 ml) and dilute to 20 ml. Evaporate 0·2 ml of the soln. in a channel of depth 7 mm and diam. 3·5 mm in a carbon electrode. Excite the spectra in a d.c. arc at 5 amp. for 1·5 min. and photograph in a glass three-prism spectrograph. As standards use synthetic soln. containing from $6·25 \times 10^{-4}$ to $2·5 \times 10^{-3}$ % of Li based on Bi. To the test soln. add an equal vol. of 1% $CsNO_3$ soln. as internal standard. A calibration graph constructed from the lines Li 6707 and Cs 7623 A is a straight line of slope $\simeq 1$. The error is 5%, and the sensitivity 5×10^{-5} %. C. D. KOPKIN

4134. **Polarographic determination of copper impurity in metallic bismuth.** D. P. Malyuga and N. V. Blyuer. *Trudy Komiss. Anal. Khim., Akad. Nauk SSSR*, 1960, **12**, 224–226; *Ref. Zhur., Khim.*, 1961, (1), Abstr. No. 1D67.—A polarographic method has been developed for the determination of Cu (10^{-3} to 10^{-4} %) in metallic bismuth after preliminary separation of Cu by pptn. with dithio-oxamide in the presence of K citrate and aq. NH_3, which maintain Bi and other elements in soln. (Malyuga, *Trudy Biogeokhim. Lab., Akad. Nauk SSSR*, 1946, **8**, 75; *Trudy Vsesoyuznyi Konf. po Anal. Khim.*, 1943, **2**, 493). *Procedure*—Dissolve 2 g of the sample in HNO_3 (1:1), first in the cold and then on a water bath, add 10 ml of 20% K, ammonium or Na citrate soln., dilute to 100 ml, make slightly alkaline to litmus with aq. NH_3, add 3 to 4 ml of 0·5% dithio-oxamide soln. and set aside for 3 hr. at room temp. Filter off the ppt. of Cu, Ni, Co, Zn and Cd dithio-oxamides, wash it with 1% NH_4Cl soln., transfer the filter to a quartz crucible, dry it, add 3 to 4 drops of conc. H_2SO_4, remove H_2SO_4 by evaporation on a sand bath, and ignite at 550° to 600°. Dissolve the residue in a few drops of conc. HCl, dilute to 10 ml with the basal soln. (0·02N-NH_4Cl and 0·1N-aq. NH_3) and polarograph. The analysis takes 8 hr.; the error is within ± 3%. C. D. KOPKIN

4135. **Determination of small amounts of lead in metallic bismuth.** S. I. Sinyakova and E. K. Gol'braikh. *Trudy Komiss. Anal. Khim., Akad. Nauk SSSR*, 1960, **12**, 187–190; *Ref. Zhur., Khim.*, 1961, (1), Abstr. No. 1D90.—The determination of small amounts ($\simeq$ 0·2%) of Pb in metallic bismuth is based on the electrolytic separation of Pb as PbO_2 and purification of the PbO_2 from Bi with thiourea. *Procedure*—Dissolve 1 g of the sample in 10 ml of HNO_3 (1:1) by heating on a water bath, add 20 ml of HNO_3 (sp. gr. 1·4), dilute to 60 ml and electrolyse at 70° to 80° for 2 hr. at 0·25 to 0·3 amp., with a platinum gauze anode (4·5 × 4 cm) and a platinum spiral cathode. After the electrolysis, wash the electrodes, dissolve the PbO_2 in 40 ml of HNO_3 (1:1) in the presence of a few drops of H_2O_2, evaporate the soln. to dryness in a quartz dish, dissolve the residue in 10 ml of N-HNO_3, saturate the soln. with thiourea until needles of $2Pb(NO_3)_2.11CS(NH_2)_2$ appear and set aside for 1 hr. at 0° (if large crystals do not form, add more thiourea at room temp.). Filter off the ppt., wash it several times with N-HNO_3 satd. with thiourea, dry it, ignite at 300° for 20 min., evaporate the residue with a few drops of HNO_3 (sp. gr. 1·4), add 1 to 2 ml of hot 20% ammonium acetate soln. and 10 ml of water and determine Pb polarographically or by the indirect iodimetric method. The error by either method is ± 7%. C. D. KOPKIN

4136. **Determination of cadmium, silver and gold impurities in metallic bismuth with dithizone.** S. I. Sinyakova and L. A. Tsvetkova. *Trudy Komiss. Anal. Khim., Akad. Nauk SSSR*, 1960, **12**, 191–205; *Ref. Zhur., Khim.*, 1961, (1), Abstr. No. 1D166.—A method is developed for determining Cd (10^{-5} %), based on the extraction of Cd dithizonate with CCl_4 from an alkaline soln. (5 to 10% NaOH, containing tartrate to complex the Bi), re-extraction of Cd with 0·1N-HCl, and colorimetry of the Cd dithizonate in a weakly alkaline medium (5 to 10% NaOH). The error of the determination is ± 11%. Silver is determined by co-extraction of Ag with Hg by means of dithizone (**I**) from HNO_3 soln. containing Bi partially complexed with tartaric acid. The Ag is re-extracted from the org. phase with NH_4SCN soln. and titrated with a soln. of **I** in CCl_4. The error is ± 10%. With a content of Ag $> 10^{-4}$ %, direct extractive titration of Ag with the **I** soln. in a basal Bi soln. is used. In the presence of large amounts of Hg and Cu, the Ag must first be separated with NH_4SCN. The error in determining Ag is ± 5·4%. A method is developed for the determination of Au by extractive titration with **I** soln. (without removal of Bi) in HCl medium. The sharpness of the colour change at the end-point is increased by the addition of Cu to the soln. C. D. KOPKIN

4137. **Determination of antimony, iron, manganese and tellurium impurities in bismuth.** S. I. Sinyakova and Ch. Ya. Krol'. *Trudy Komiss. Anal. Khim., Akad. Nauk SSSR*, 1960, **12**, 206–216; *Ref. Zhur., Khim.*, 1961, (1), Abstr. No. 1D167.—In determining Mn and Fe in bismuth the methods used are based on colorimetry of MnO_4^- (after oxidation with persulphate) and of the complex of Fe^{3+} with SCN^- extracted with isoamyl alcohol. The error for Fe (20 to 50 μg) is ± 4·2%, and for Mn (2 to 50 μg), ± 8·5%. It is shown that Bi does not interfere in the colorimetric determination of Sb with rhodamine B (error ± 7·7%); in determining Sb by the iodide - pyridine method, it is first separated by co-pptn. with Sn as the meta-acids. To 1 g of sample add $Sn(SO_4)_2$ soln. containing $\simeq$ 1 mg of Sn and 5 ml of HNO_3 (1:1), boil to dissolve the bismuth and remove oxides of N, add 6 ml of water, boil for a further 10 to 15 min., transfer the soln. to a centrifuge tube, set aside for 2 to 3 hr. (for the pptn. of the meta-acids) and centrifuge. Wash the ppt. (× 4 or 5) with hot 10% HNO_3, dissolve it by heating with 2 or 3 drops of conc. H_2SO_4, and determine Sb by the iodide - pyridine method. The error is ± 8·8%. A method is developed for the determination of Te, based on colorimetry of the tellurium metal sol obtained by reduction with $SnCl_2$ soln. in 2·2N-HCl. Dissolve 2 g of sample in 20 ml of conc. HNO_3, evaporate to dryness, add 3 ml of conc. HCl and again evaporate. Add a further 3 ml of conc. HCl, heat to dissolve the residue, cool, wash the soln. into a colorimeter cylinder with 2% HCl (2 to 3 ml), dilute to 10 ml, add 1 ml of 10% $SnCl_2$ soln., set aside for 10 min., and compare the resulting brown colour with those of standard soln. containing 10 to 30 μg of Te and 2 g of Bi treated in the same way. The error for 10^{-3} % of Te is ± 2·8%. C. D. KOPKIN

4138. **Spectrophotometric determination of vanadium(V) with *N*-benzoyl-*N*-phenylhydroxylamine.** U. Priyadarshini and S. G. Tandon (Dept. of Chem., Jabalpur Univ., India). *Anal. Chem.*, 1961, **33** (3), 435–438.—This highly specific procedure is based on an extraction into $CHCl_3$ of the deep-violet H_2O-insol. complex of V^{5+} with *N*-benzoyl-*N*-phenylhydroxylamine (0·1%) in 2·8N to 4·3N-HCl at 20° to 40°. The extinction is measured at 510 mμ against that of $CHCl_3$; Beer's law is followed between 0·7 and 12 p.p.m. of V. The aliquot of the sample soln. should contain 0·02 to 0·2 mg of V^{5+}, and the final vol. should be 25 ml. The effect of variables on the development of the colour, and the control of interferences by standard methods are discussed. The sensitivity is 0·011 μg of V per sq. cm. W. J. Baker

4139. **Spectrophotometric determination of niobium with ascorbic acid.** G. E. Janauer and J. Korkisch (Anal. Inst., Univ. Wien, Austria). *Anal. Chim. Acta*, 1961, **24** (3), 270–275 (in German).—The yellow complex formed by Nb with ascorbic acid (**I**) follows Beer's law over a wide range of concn. *Procedure*—The sample is fused with K_2CO_3, dissolved in 100 ml of H_2O and 1 ml of this soln. (≡20 to 400 μg of Nb) is added to 0·5 g of **I** in a 10-ml flask, followed by 1 ml of 2·5M-Na acetate, 0·6 ml of N-HCl and ≃ 2 ml of H_2O. The flask, together with a blank flask (containing Na acetate soln. and **I**, but no HCl), is placed in a vacuum desiccator and evacuated for 1 hr. Finally, the soln. are diluted to vol. and the extinctions measured at 345 mμ after 10 min.; the error is within ± 4%. Serious interference is caused by PO_4^{3-}, Br^-, F^-, UO_2^{2+}, V, Mo and Ti. Tantalum can be similarly determined at 330 mμ, but the sensitivity is low.
P. D. Parr-Richard

4140. **Direct determination of niobium and tantalum with the anionic exchanger Wofatit SBW.** S. Spauszus and M. Heimer (Dtsch. Amt für Material u. Warenprüf. Prüfdienststelle, Magdeburg, Germany). *Chem. Tech., Berlin*, 1961, **13** (2), 96–99.—In the analysis of alloy steels for Nb and Ta, direct gravimetric determination of each of these elements (as oxide) is made possible by an ion-exchange separation of the Nb and Ta after removal of W. *Procedure*—The mixture of the potassium salts of the acids of Nb, Ta and W (obtained from the steel by a usual method, described) is treated in soln. at 50°, first with a soln. containing 80 g of NH_4Cl and 80 ml of aq. NH_3 (sp. gr. 0·91) per litre and then with a soln. containing 40 g of $MgSO_4.7H_2O$ in 900 ml of water, thereby pptg. Nb and Ta. The pptd. salts are dissolved, and freed from Mg by treatment with benzenearsonic acid soln., and the pptd. niobate and tantalate is ignited. The ash is fused with $K_2S_2O_7$, and the melt is dissolved in a mixture (*A*) containing 740 ml of HCl and 2·5 ml of HF (40%) per litre; the soln. is run slowly into the ion-exchange column, which is eluted with soln. *A* to obtain first an eluate of Nb free from Ta and then an eluate of Ta free from Nb; each eluate is treated (by a series of steps described) to obtain an ashed oxide. If the steel contains Ti, each of the final ashed oxides will be contaminated by titanium oxide, rendering necessary a correcting (colorimetric) determination of Ti, or a separation of Ti (with selenous acid). H. L. Whitehead

4141. **Spectrographic determination of niobium and zirconium in ores, concentrates and tailings.** P. D. Korzh and V. E. Pererva (Magnitogorsk Mining Metallurgy Inst.). *Zavod. Lab.*, 1961, **27** (3), 311–312.—The sample, mixed with graphite powder, is excited in an a.c. arc; Nb_2O_5 and ZrO_2 are determined over the range 0·01 to 10% and 0·01 to 12%. G. S. Smith

4142. **Determination of lead, bismuth, tin and cadmium in niobium and niobium alloys.** Z. S. Mukhina, A. A. Tikhonova and I. A. Zhemchuzhnaya. *Trudy Komiss. Anal. Khim., Akad. Nauk SSSR*, 1960, **12**, 71–74; *Ref. Zhur., Khim.*, 1961, (1), Abstr. No. 1D159.—A method has been developed for the determination of Pb (> 10^{-4} %), Bi (> 10^{-5} %), Cd (> 10^{-4} %) and Sn (> 10^{-4} %). *Procedure*—Dissolve 5 g of metallic niobium in 50 ml of HF in a platinum dish, add HNO_3 (1:1) towards the end of the dissolution, then 30 to 40 ml of HF; evaporate to 10 to 15 ml, and transfer to a 700-ml conical flask containing 16 g of H_3BO_3, 200 ml of water and 80 ml of a 50% tartaric acid or Na citrate soln; add aq. NH_3 till the soln. is alkaline to Congo red, and then acidify with H_2SO_4 (1:1) and add 5 ml in excess for each 100 ml of soln., heat and pass H_2S. After 30 min. add 100 ml of aq. H_2S soln. to complete the pptn. of Cd and pass H_2S for a further 30 min. Allow the ppt. to settle, filter, wash the ppt. 8 times with H_2S soln., dissolve it in a mixture of HCl and HNO_3, add 3 g of Al (as $AlCl_3$) and precipitate Pb, Sn and Bi and trace amounts of Fe with aq. NH_3. Determine Cu and Cd in the filtrate polarographically (Cu in an ammoniacal basal soln.). Cadmium can also be determined with dithizone after removal of Cu by electrolysis with a platinum cathode. Dissolve the hydroxides of Pb, Sn and Bi in a mixture of 10 ml of HNO_3 (1:1) and 5 ml of H_2SO_4 (1:5). Precipitate Sn with MnO_2 by the Blumenthal method and determine it polarographically in a basal soln. of 6N-HCl (the sensitivity is increased by using a 10-g sample or by combining the soln. from two 5-g samples and making the final vol. up to 15 ml). After removal of Sn, precipitate Pb in the filtrate with aq. NH_3 and determine it polarographically in a basal soln. of 6N-HCl or 10% ammonium tartrate (pH 8). Determine Bi colorimetrically by means of the iodine - bismuth or the thiourea complex. Lead and Bj can also be determined by the dithizone method.
C. D. Kopkin

4143. **Identification of phosphate anions in niobium and tantalum phosphates by means of infra-red spectra.** S. Z. Haider (Dept. of Chem., Dacca Univ., Pakistan). *Anal. Chim. Acta*, 1961, **24** (3), 250–253 (in English).—Spectra of the compounds $Nb_2O_5.2P_2O_5$, $Mg_2P_2O_7$, ZrP_2O_7, $NbO.PO_4$, $TaO.PO_4$ and $Ta_2O_5.3P_2O_5$ were recorded from 600 to 4000 cm^{-1} and compared with those of reference materials; identification of the groups $P_2O_7^{4-}$, PO_4^{3-} and $P_3O_{10}^{5-}$ was possible.
P. D. Parr-Richard

4144. **Procedures for the isolation of tantalum isotopes produced by deuteron bombardment of tungsten.** A. Demildt and J. Hoste (Lab. de Chim. Anal., Ghent Univ., Belgium). *Bull. Soc. Chim. Belg.*, 1961, **70** (3–4), 145–153 (in English).—Three procedures are given for the carrier-free separation of ^{182}Ta, ^{183}Ta and ^{184}Ta from W, Re and Nb after dissolution of the target. (*i*) By adsorption on $Fe(OH)_3$, making three pptn., followed by dissolution of the ppt. and removal of Fe by extraction with isoamyl acetate; the

yield is $\simeq$ 80% and the decontamination factor $\simeq 5 \times 10^5$. (*ii*) By proceeding as in (*i*), making only one pptn. of $Fe(OH)_3$, and then passing the tantalum soln. through a 45-cm column of Dowex 1-X8 and eluting with 2M-HCl - 0·01M-oxalic acid at 25° (the fraction between 3 and 6 column-vol. contains Ta); the yield is $\simeq$ 50%. (*iii*) By liquid - liquid extraction of the prepared soln. with either di-isopropyl ketone (**I**) or di-isobutyl ketone (**II**) equilibrated with M-HF - 6M-HCl at 20°, followed by back-extraction of Ta into H_2O; the recovery is $\simeq$ 95% with **I** and 70% with **II**, but is much lower in the presence of Ta carrier (10 mg). In all three procedures Na_2WO_4 is added as hold-back carrier. The radio-isotopes of Ta can be identified by their decay curves and measured β- and γ-energies (listed).

W. J. Baker

4145. **Coulometric analyser for trace quantities of oxygen.** F. A. Keidel (E. I. du Pont de Nemours and Co., Inc., Wilmington, Del., U.S.A.). *Ind. Eng. Chem.*, 1960, **52**, 490–493.—An instrument is described for measuring small quantities of free O. The range is given as 1 p.p.m. to 1% by vol. in gases and 10 p. per 10^9 to saturation in liquids.

Chem. Abstr.

4146. **Physico-chemical methods for determining the forms of sulphur in aqueous solutions [from petroleum].** L. P. Petrova. *Trudy Vses. Nauch.-Issled. Geol.-Razved. Inst.*, 1960, (155), 329–340; *Ref. Zhur., Khim.*, 1961, (1), Abstr. No. 1D132.—To determine $< 5 \times 10^{-3}$ % of SO_4^{2-} in petroleum waters, amperometric titration with $Pb(NO_3)_2$ soln. is used. Interference by Cl^- can be eliminated by adding ethanol to 30% by vol. The error is 1 to 2%. With a Cl^- to SO_4^{2-} ratio $< 40:1$, it is recommended to determine SO_4^{2-} by the indirect polarographic method from the decrease in the height of the Ba wave. The accuracy of the determination depends on the relative concn. of SO_4^{2-} and $BaCl_2$. The applicability of Gerber's method (*Zhur. Anal. Khim.*, 1947, **2** (5)) for determining S^{2-} in petroleum waters is shown. Potentiometric titration with a bimetallic electrode pair in an uncompensated circuit by Miller's method (*Ref. Zhur., Khim.*, 1955, (7), Abstr. No. 11,903) has been used to determine S^{2-}, $S_2O_3^{2-}$ and SO_3^{2-}. The error is 4%.

C. D. Kopkin

4147. **Micro-method for the determination of hydrogen sulphide.** E. A. Delwiche (Coll. of Agric., Cornell Univ., Ithaca, N.Y.). *Anal. Biochem.*, 1960, **1** (4–5), 397–401.—The photometric procedure described for the determination of soluble S^{2-} in the range 10 to 100 μg is based on the pptn. of colloidal PbS, stabilised with gum acacia. A calibration curve is prepared by using Pb acetate and Na_2S. The method is simple, convenient and rapid, and is useful for large numbers of determinations. Trichloroacetic acid interferes.

F. Powell

4148. **The significance of R_M values for the paper chromatography of ammonia derivatives of sulphuric acid.** G. Kempe (Inst. f. Anorg. Chem., Tech. Hochsch. f. Chem., Leuna-Merseburg, Germany). *Z. anal. Chem.*, 1961, **180** (1), 9–14 (in German).—For this purpose, R_M is defined as log $(R_F/1-R_F)$; 8 compounds, members of 3 homologous series, were separated on S. & S. 2043a paper. The ascending method was used with dioxan - H_2O - conc. aq. NH_3 (68·5:31·4:0·1) as solvent. Spots were detected as described previously (*Anal. Abstr.*, 1958, **5**, 4077). R_F values are given for the diamides, $H(HNSO_2)_nNH_2$, the amido-sulphonic acids, $H(HNSO_2)_nOH$ and the disulphonic acids, $HO_3S(HNSO_2)_nOH$. In each series, as n increases, the R_F decreases. Between the series, for equal n values, the R_F decreases in the order given. This is associated with the hydrophilic nature of the $-SO_3H$ groups. For each additional $HNSO_2$ group, there is an identical decrease in R_M in the 3 series. By using this value ($\triangle R_M = -0{\cdot}47$) certain other R_M values are derived, *e.g.*, the substitution of –OH by $-NH_2$ leads to an increase in R_M of 0·74 and the substitution of –H by $-SO_3H$ leads to an increase of 0·21. In 10 different chromatograms, with NH_2SO_3H as a standard, R_F values for 5 other compounds were calculated in this way. Differences between calculated and observed R_F values rarely exceeded 0·02.

G. Russell

4149. **Colorimetry of sulphur anions. I. An improved colorimetric method for the determination of thiosulphate.** P. J. Urban (Govt. Metallurg. Lab., Univ. of Witwatersrand, Johannesburg, S. Africa). *Z. anal. Chem.*, 1961, **179** (6), 415–422 (in English).—With a $CuCl_2$ catalyst, $S_2O_3^{2-}$ are converted into SCN^-, which are determined with Fe^{3+}. Interference by polythionates is avoided by working at pH 5. *Procedures:* (*i*) *With polythionates absent*—Transfer a neutral aliquot (0·1 to 2 mg of $S_2O_3^{2-}$) to a blackened 100-ml flask and dilute to $\simeq$ 50 ml. Add 1% NaCN soln. (5 ml) and then, with rapid swirling, 0·1M-$CuCl_2$ (3 ml). Then add Fe^{3+} soln. [$Fe(NO_3)_3.9H_2O$ (300 g), 55% HNO_3 (400 ml), and water to 1 litre] (5 ml) and dilute to 100 ml. Prepare a blank with 50 ml of water. If free SCN^- are present, prepare a sample blank as described above but adding the $Fe(NO_3)_3$, $CuCl_2$ and NaCN soln. in that order. The colour (measured at 460 mμ) is stable for at least 2 hr. in the blackened flasks. (*ii*) *With polythionates present*—Transfer an aliquot to a 125-ml beaker, dilute to $\simeq$ 30 ml and add 10% (v/v) acetic acid (1 ml). Add aq. NH_3 (1:9) or 10% acetic acid in a vol. (previously determined) such that, after addition of 1% NaCN soln. (5 ml) the pH is 5·0 $\pm$ 0·2. Add, with rapid stirring, $CuCl_2$ soln. (3 ml) immediately after the NaCN, then $Fe(NO_3)_3$ soln. (5 ml). Transfer at once to a blackened 100-ml flask and proceed as described above. If free SCN^- are present, prepare a sample blank by adding $Fe(NO_3)_3$, NaCN and $CuCl_2$ in that order; 10 mg of $K_2S_4O_6$ or 30 mg of $K_2S_2O_6$. $K_2S_5O_6$ or $K_2S_6O_6$ does not interfere, but S^{2-} do. A transmittancy lower by $\simeq$ 1 to 2% is obtained in the calibration curve in procedure (*ii*).

II. A specific colorimetric method for the determination of trithionate. P. J. Urban. *Ibid.*, 1961, **179** (6), 422–426 (in English).—The conversion of $S_4O_6^{2-}$, $S_5O_6^{2-}$, $S_6O_6^{2-}$ and $S_2O_3^{2-}$ into SCN^- with a $CuCl_2$ catalyst is very rapid ($< 1{\cdot}5$ min.), whereas that of $S_3O_6^{2-}$ is slow ($k = 2{\cdot}7 \times 10^{-4}$ per sec. at 24°); determinations of the SCN^- formed after 2 min. and after 16 hr. can thus be used to determine the $S_3O_6^{2-}$. *Procedure*—Transfer 2 neutral aliquots to blackened 100-ml flasks and dilute to $\simeq$ 50 ml. Add 5% NaCN soln. (5 ml) and mix. After 2 min., stop the reaction in the first sample by adding 0·2M-$CuCl_2$ (5 ml) with rapid swirling. Wash down and immediately add $Fe(NO_3)_3$ - HNO_3 soln. (5 ml), dilute to vol. and measure at 460 mμ. After 16 hr. treat the second sample in the same way. Prepare a fresh reagent

blank, without $CuCl_2$, for each aliquot. The SCN^- calculated from the difference between the two readings corresponds to 98·4% of the $S_2O_6^{2-}$. It is convenient to prepare a calibration curve from 0·002N-NH_4SCN covering the range 0·1 to 1·2 mg of SCN^-. Determinations in the presence of $S_4O_6^{2-}$ gave an error of $< \pm 2\%$. G. RUSSELL

4150. **Determination of thiosulphates by sodium hypobromite in alkaline solution.** A. Claeys and H. Sion (Lab. de Chim. Anal., Ghent Univ., Belgium). *Bull. Soc. Chim. Belg.*, 1961, **70** (3–4), 154–161 (in French).—At low concn. ($\simeq$ 0·01M), $S_2O_3^{2-}$ can be determined to within $\simeq$ 0·4% by adding an excess of KOBr soln. and titrating the excess with $Na_2S_2O_3$ at 25°. The stable soln. of 0·1N-KOBr is prepared from KBr - $KBrO_3$ and is standardised iodimetrically with $Na_2S_2O_3$. *Procedure*—To the KOBr soln. (50 ml) add 2N-NaOH (2 ml), followed by the sample soln. (25 ml). After 1 hr. add 20% aq. KI (6 ml) and 6N-H_2SO_4 (25 ml) and titrate immediately with $\simeq$ 0·1N-$Na_2S_2O_3$ soln., with starch as internal indicator. W. J. BAKER

4151. **Mercurimetric titration of thiosulphate and sulphide in the presence of dithionite.** M. Wroński (Inst. Chem. Technol., Univ., Łódź, Poland). *Z. anal. Chem.*, 1961, **179** (5), 350–351 (in German).—Incorrect values for thiosulphate in technical dithionite, given by the iodimetric method, are avoided by direct titration with *o*-hydroxymercuribenzoic acid (**I**), which is prepared as a 0·05N soln. by dissolving 16 g of the acid anhydride in 0·1N-NaOH (100 ml) and diluting to 1 litre, and standardised against thiosulphate. *Procedure for sulphide*—Treat the sample (containing > 1 g of $Na_2S_2O_4$) with N-NaOH (5 ml), dilute to 100 ml, add 0·1% ethanolic dithizone soln. (0·5 ml) and titrate at once with the **I** soln. to a sharp colour-change from yellow to red. The mean error is $\pm$ 0·2%. *Procedure for thiosulphate*—Dissolve 0·2 g of sulphide-free sample in 5% formaldehyde soln. (10 ml), add N-NaOH (0·5 ml), dilute to $\simeq$ 60 ml, add 10% NaH_2PO_4 soln. (2 ml) and titrate with **I** soln. to a violet end-point, with 0·5% diphenylcarbazone soln. (1 ml) as indicator. If the soln. is red owing to alkalinity, add more NaH_2PO_4. The error is $\pm$ 0·8%. G. RUSSELL

4152. **Determination of trace impurities in high-purity selenium.** A. I. Williams (Nat. Phys. Lab., Teddington, Middx., England). *Analyst*, 1961, **86**, 172–177.—Neutron-activation methods are described for the determination of trace amounts of Cd, Cu, Ni, Te and Zn. The sample is irradiated with 10^{12} neutrons per sq. cm per sec. for 24 hr., then dissolved in HNO_3 in the presence of a carrier of the element being determined. By methods described in detail and appropriate to each element they are separated, Cd as the phosphate, Cu as cuprous thiocyanate, Ni as the glyoxime complex, Te as the element and Zn as the double salt with mercuric thiocyanate. The separated ppt. is dried, weighed and counted. The activities of the sample ppt. are compared with those of standards irradiated simultaneously with the sample and, after dissolution and addition of carrier, pptd. under the same conditions as the sample. A. O. JONES

4153. **Polarographic determination of tellurium in copper and lead compounds.** A. I. Zelyanskaya and L. S. Gorshkova. *Trudy Inst. Metallurg., Ural'sk. Fil. Akad. Nauk SSSR*, 1960, (5), 141–144; *Ref. Zhur., Khim.*, 1961, (1), Abstr. No. 1D135.—In the polarographic determination of Te in copper-containing products, Cu is first removed on the cationite Wofatit R (NH_4^+ form). Quant. separation of Te from Cu is attained in ammoniacal soln. ($\simeq$ 10% aq. NH_3) containing 5 ml of a satd. $Na_4P_2O_7$ soln. as complexing agent for Fe, with a flow-rate of 6 to 8 ml per min. Evaporate the percolate to $\simeq$ 25 ml, dilute to 50 ml with ammoniacal basal soln. (N-aq. NH_3, N-NH_4Cl, 40 g of Na_2SO_3 per litre, 0·1% of gelatin) and polarograph. In this basal soln. Te forms a clearly developed wave ($E_{\frac{1}{2}} = -0{\cdot}9$ V *vs.* the S.C.E.); Se does not interfere. With high Cu concn. the analysis takes 4 to 6 hr. To determine Te in lead-containing products, boil the filtrate after dissolution of the alloy, add 20% $SnCl_2$ soln. to reduce Fe and a further 3 to 5 ml for complete pptn. of Te or total Te plus Se, and set the soln. and ppt. aside for 3 to 4 hr. on a warm plate or for $\simeq$ 12 hr. at room temp. Filter off the ppt., wash it with hot 1 to 2% HCl, transfer the filter and ppt. to a 250-ml flask, dissolve the ppt. in 5 ml of HCl and 3 to 5 drops of HNO_3, and neutralise to Congo red with aq. NH_3. Cool, dilute to 50 ml with the ammoniacal basal soln., and polarograph. C. D. KOPKIN

4154. **Determination of chromium in minerals.** A. de Sousa (Rua Rodrigo da Fonesca 190–3E, Lisbon 1, Portugal). *Chemist Analyst*, 1961, **50** (1), 9–11.—After oxidation to Cr^{VI}, the Cr is pptd. as $BaCrO_4$. The ppt. is dissolved with HCl and KI and the Cr is reduced to Cr^{III}. The Cr is then pptd. as $Cr(OH)_3$, and the Ba in the filtrate is titrated with standard EDTA soln. *Procedure*—The sample (1 g) is fused with 8 g of Na_2O_2 in an iron crucible, and the melt is extracted with 100 to 150 ml of H_2O. The excess of peroxide is destroyed by boiling, 10 to 15 g of ammonium carbonate is added and the soln. is filtered. The filtrate is just acidified with acetic acid or HCl and 10 ml of 0·5M-$BaCl_2$ is added dropwise. After 1 hr. on a steam bath the soln. is filtered through a Gooch crucible and the ppt. is washed five times with ethanol - water (1:9). The contents of the crucible are dissolved in 100 ml of HCl (1:1) containing 2 g of KI, and the Cr is pptd. with aq. NH_3. The filtrate and washings are diluted with an equal vol. of ethanol, and 2 to 3 drops of *o*-cresolphthalein complexone (0·1% aq. soln., faintly ammoniacal) per 100 ml and 2 ml of conc. aq. NH_3 are added. The soln. is titrated immediately with 0·1M-EDTA until the red colour is abruptly discharged. The procedure takes $\simeq$ 4 hr. J. H. WATON

4155. **Determination of the chromium trioxide - sulphate ratio in chromium plating baths.** M. A. Shluger and V. A. Kazakov. USSR Pat. 133,311 (10.11.1960).—The time from the switching on of the polarising current to the sharp change of potential is used to determine the ratio of CrO_3 to SO_4^{2-} from a calibration curve. The cathode is a copper wire of cross-section 1 sq. mm fused in glass, the anode a brass plate, 3 mm × 4 mm, covered with a thick layer of chromium; the c.d. is usually 8 to 10 amp. per sq. dm. The time interval depends on the actual CrO_3 content and is practically independent of the Cr^{III} content. C. D. KOPKIN

4156. **Determination of traces of lead, tin, bismuth and cadmium in metallic chromium and its alloys.** Z. S. Mukhina, A. A. Tikhonova and I. A. Zhemchuzhnaya. *Trudy Komiss. Anal.*

Khim., Akad. Nauk SSSR, 1960, **12**, 298–310; *Ref. Zhur., Khim.*, 1961, (1), Abstr. No. 1D160.—The elements named are precipitated with H_2S in dilute H_2SO_4 medium (pH 3) or are co-precipitated with methyl violet iodide. To increase the sensitivity and accuracy, Cr is removed as $CrOCl_2$. Lead and Cd are determined polarographically, or colorimetrically with dithizone, Sn polarographically in a basal soln. of 6N-HCl, and Bi colorimetrically by means of the iodine - bismuth complex. The sensitivity is 10^{-4} % for Pb, Sn and Cd, and 10^{-5} % for Bi. C. D. KOPKIN

4157. **Determination of antimony impurity in pure chromium and its alloys.** E. I. Nikitina. *Trudy Komiss. Anal. Khim., Akad. Nauk SSSR*, 1960, **12**, 311–313; *Ref. Zhur., Khim.*, 1961, (1), Abstr. No. 1D129.—A method for determining 0·0002 to 0·1% of Sb is based on extraction, with toluene, of the compound of Sb with methyl violet, followed by photometry. *Procedure*—Dissolve the sample (≃ 0·5 g) by heating with a mixture of 10 ml of H_2SO_4 (1:5) and 20 ml of HCl (1:1), transfer to a 200-ml cylinder, add 5 ml of HCl (sp. gr. 1·19) and 1 ml of 10% $NaNO_2$ soln. (to oxidise Sb^{3+} to $SbCl_6^-$), stir for 5 min., add 0·5 ml of satd. urea soln., 40 ml of water (without stirring) and 10 drops of 0·2% methyl violet soln.; shake the soln. rapidly three times, add 30 ml of toluene, shake for 2 min. in a separating-funnel, remove the org. layer and measure the extinction with a green filter in a 3-cm cell. C. D. KOPKIN

4158. **Photometric determination of molybdenum-(V) with 8-hydroxyquinoline-5-sulphonic acid.** A. I. Busev and Fan Chang (School Anal. Chem., Moscow Univ.). *Vestn. Moskov. Univ., Ser. Khim.*, 1961, (2), 36–40.—On heating 8-hydroxyquinoline-5-sulphonic acid (**I**) with Mo^V a stable red complex with an absorption max. at 540 mμ is formed. *Procedure*—To 10 ml of a weakly acid soln. containing 0·15 to 0·65 mg of Mo add 5 ml of **I** soln. (dissolve 2·3 g of **I** in 100 ml of H_2O by adding NaOH soln., filter, and neutralise with HCl), 20% hydrazine hydrochloride soln. (1·5 ml) and acetate buffer (pH 3·6) (10 ml) and heat on a water bath for 15 to 25 min. Cool, dilute to 50 ml and measure the extinction at 540 mμ. In the presence of large amounts of W^{VI} add 10 to 15 ml of **I** soln. Magnesium, Ca, Ba, Ni, Cd, Al, Mn^{2+}, Cr^{3+} and small amounts of Bi, Cu and U do not interfere; Co, Zn, V, Fe^{3+}, large amounts of Cu, EDTA and tartaric acid do. J. W. PRICE

4159. **New spectrophotometric method for molybdenum.** A. H. Black and J. D. Bonfiglio (Toledo Univ., Ohio, U.S.A.). *Anal. Chem.*, 1961, **33** (3), 431–432.—From 0·1 to 0·5% of Mo in low-alloy steel can be determined rapidly by passing the pre-treated acid soln. (pH 2) of the sample slowly through a 15-cm column of Amberlite IR-120 (H^+ form, 50 to 100 mesh) and allowing the percolate to flow into a 0·1% (w/v) soln. of phenylfluorone in methanol. The extinction of the resulting orange - red Mo - phenylfluorone complex is measured at 550 mμ; Beer's law is followed over the range of 0·33 to 1·67 μg of Mo per ml. Complete removal of Mo from the resin is assured by addition of citric acid (50 mg) to the initial soln., which must contain $(NH_4)_2SO_4.FeSO_4$ to reduce any CrO_4^- or VO_3^-. The percolate is free from interfering ions. W. J. BAKER

4160. **Determination of impurities in molybdenum and its compounds.** A. G. Karabash, Z. N. Samsonova, N. I. Smirnova-Averina and Sh. I. Pelzulaev. *Trudy Komiss. Anal. Khim., Akad. Nauk SSSR*, 1960, **12**, 255–264; *Ref. Zhur., Khim.*, 1961, (1), Abstr. No. 1D163.—Molybdenum and its compounds are converted into MoO_3 and mixed with an equal amount of carbon powder containing 30% of Ga_2O_3. The spectrum is excited in a d.c. arc. Magnesium, Ca, Ba, Al, Cr, Mn, Fe, Co, Ni, Cu, Ag, Cd, Pb, Sb and Bi are determined from one spectrogram with a sensitivity of 10^{-3} to 10^{-5} %. The relative error is ± 20%. Silicon is determined in a separate sample that has been converted to MoO_3 by ignition at 600° in a beryllia crucible. Two methods are described for the concentration of the impurities. C. D. KOPKIN

4161. **Colorimetric determination of free carbon in molybdenum and tungsten carbides.** T. N. Nazarchuk and L. E. Pechentkovskaya (Inst. of Metallo-Ceramics and Special Alloys, Acad. Sci., UkrSSR). *Zavod. Lab.*, 1961, **27** (3), 256–258.—The method is a modification of that described by Popova and Zaslavskaya (*Anal. Abstr.*, 1956, **3**, 1367). G. S. SMITH

4162. **Polarographic behaviour of the heteropoly-acids of molybdenum. III. Polarography of molybdogermanic acid.** K. Grasshoff and H. Hahn (Chem. Inst., Univ., Würzburg, Germany). *Z. anal. Chem.*, 1961, **180** (1), 18–31 (in German).—Molybdogermanic acid (prep. described) is polarographically reducible; at pH 4 well-formed waves are given. With the cathode-ray polarograph there are five peaks, the first and last corresponding to the reduction of Mo. The middle peak (−0·45 V *vs.* the S.C.E.) is recommended for the quant. determination. *Procedure*—Treat the sample soln. (100 to 1000 μg of Ge) with 1% $Na_2MoO_4.2H_2O$ soln. (5 ml). Adjust the pH to 2·0 ± 0·1 with 0·2N-HCl. Dilute the soln. to 100 ml with HCl (pH 2), heat on a water bath for 2 hr., then set aside overnight at room temp. Dilute an aliquot (5 ml) to 25 ml with supporting electrolyte [0·1M-Na acetate, 0·5M-acetic acid, 0·1M-NaCl, citrate buffer (pH 3·6) (100 ml), and ethyl methyl ketone (80 ml) per litre]. De-oxygenate and record the polarogram. The calibration curve is linear for concn. up to 1 μg of Ge per ml. The coeff. of variation of the peak current over the concn. range quoted was 1·6% (84 measurements). G. RUSSELL

4163. **Spectrographic analysis of tungsten for the content of impurities.** V. S. Moleva and Sh. I. Pelzulaev. *Zavod. Lab.*, 1961, **27** (3), 309–310.—The determination of 15 elements from the same spectrogram is described. One part of the sample (0·5 g) is ignited at 800° to 850° to WO_3, and another part (1 to 2 g) is subjected to hydrochlorination, the residue is ignited at 400° and the coefficient of enrichment of impurities (quantitative concentration of Mg, Al, Ca, Ba and Mn and partial concentration or complete loss of the other elements) is determined by weighing. The two parts are mixed in the ratio 2:1 with a buffer mixture of carbon and silver (4:1), the silver serving to stabilise the d.c. arc and to facilitate uniform entry of the impurities into the discharge. G. S. SMITH

4164. **Sensitive method for detection and semi-quantitative determination of uranium.** Z. Šulcek, J. Michal and J. Doležal (Dept. of Anal. Chem.,

Charles' Univ., Prague, Czechoslovakia). *Chemist Analyst*, 1961, **50** (1), 13–14.—The rapid and simple method described is based on the intense fluorescence in u.v. light of uranyl ions adsorbed on a silica-gel column. *Procedure*—The column consists of a tube (10 cm × 3·5 mm) narrowed at the lower end and fitted with a glass-wool plug. Silica gel (0·08 to 0·18-mm mesh), previously washed with 0·1M-NH_4Cl (pH 9·5), is added to a height of 3 to 4 cm. The sample soln. (1 to 500 ml containing < 1 μg of U) is made 0·1M with respect to NH_4Cl, and 1 to 30 ml of 0·2M-EDTA (disodium salt) is added; tartrate should be added if a ppt. is still given by aq. NH_3. The soln. is brought to pH 8·5 to 9·5 with aq. NH_3, and is passed through the column at a rate of 30 ml per hour. The column is washed with de-mineralised H_2O, and the fluorescence of the U adsorbed in a narrow zone 1 to 3 cm from the top is observed under u.v. light. For a semi-quant. determination, a tube 5 mm in diam. is used, with a flow-rate of 2 ml per hr. The fluorescence is compared with that of standards in the range 5 to 100 μg. The error is $< 40\%$, and 0·001% of U can be determined in a 1-g sample. The limit of detection is < 1 μg of U, and the dilution limit > 1 in 5×10^7. No interference is given by an excess of Sn, Ti, Th or Zr or usual amounts of Be.

J. H. Waton

4165. **Colorimetric determination of uranium in phosphate rock after extraction with alkyl acid phosphates.** W. B. Smith and J. Drewry (Marchon Products Ltd., Whitehaven, Cumb., England). *Analyst*, 1961, **86**, 178–184.—The sample (5 g) is dissolved in HCl (1:1) with additions of $KClO_3$. Aq. cupferron soln. (1%) is added to the diluted, cooled, filtered soln. and the Fe is removed by repeated extraction with $CHCl_3$. To the aq. liquid are added 5 ml of aq. hydroxyammonium chloride soln. (10%), NaCl (10 g) and ethanol (50 ml) and the mixture is extracted twice with a soln. in light petroleum of lauryl acid phosphate (prep. described). The separated organic layer is washed with a mixture of HCl, ethanol and hydroxyammonium chloride soln., then evaporated to dryness, and the organic matter is destroyed by heating with H_2SO_4 and HNO_3. The residue is heated to fuming with HNO_3 and $HClO_4$, then boiled with water, made alkaline with NaOH and then just acid with H_2SO_4. After addition of Na_2CO_3 soln. the liquid is boiled, digested just below b.p. for 5 min. and filtered hot. To the filtrate is added 5N-NaOH (1 ml) and the liquid is diluted to 50 ml. The extinction is measured against water in a Spekker absorptiometer, with No. 1 and OV1 filters, then 1 ml of H_2O_2 is added and after formation of the yellow colour the extinction is measured again. The difference between the two extinctions is referred to a calibration graph. The method is applicable to crude H_3PO_4.

A. O. Jones

4166. **The extraction of uranium(VI) complexes with dibenzoylmethane.** V. Moučka and J. Starý (Inst. Nucl. Chem., Czech. Tech. High School, Prague). *Coll. Czech. Chem. Commun.*, 1961, **26** (3), 763–771 (in German).—The dissociation const., partition coeff., and solubility of dibenzoylmethane (**I**) in H_2O, CCl_4, $CHCl_3$ and benzene are determined spectrophotometrically. The extraction of U^{VI} from H_2O by **I** into these solvents is dependent on pH, dissociation being complete above pH 11·3 and noticeable above pH 7, and on the concn. of U and **I**. A comparison of the values for **I** with those for acetylacetone and benzoylacetone shows that as the partition coeff. of the chelating agent increases so does that of the complex.

J. P. Stern

4167. **Polarography of large amounts of uranium.** B. P. Melent'ev and N. S. Gertseva. *Trudy Inst. Metallurg., Akad. Nauk SSSR*, 1960, (5), 198–201; *Ref. Zhur., Khim.*, 1961, (1), Abstr. No. 1D106.—The possible polarographic determination of large amounts of U is studied. On a dropping-mercury electrode in a basal soln. of 9M-NaOH containing 6% of mannitol (72 g of NaOH dissolved in 100 ml of water and 12 g of mannitol added to the hot soln.), U gives a wave at $E_{\frac{1}{2}} \simeq -0{\cdot}95$ V *vs.* the mercury anode, which can be used to determine 10 to 2000 mg of U per litre with an error of 2 to 3%. At U concn. of 1 to 10 mg per litre the errors are greater, because of the polarographic activity of the basal soln. The form of the U wave becomes less satisfactory as the U concn. increases. No interference is caused by Cu or Cr, or by Fe if the ratio of U to Fe is $> 10:1$. In a basal soln. of 50% diammonium hydrogen citrate, U gives a wave at $E_{\frac{1}{2}} \simeq -0{\cdot}6$ V, which can be used to determine 50 mg to 9 g of U per litre. At U concn. of > 4 g per litre the polarogram has a maximum, the height of which increases with increasing U concn. The method of derivative polarography can be used to determine up to 15 g of U per litre. The maximum, which appears as a minimum on the derivative polarogram, appears at U concn. of > 9 g per litre, but does not interfere in the determination, since it lies beyond the U peak. No interference is caused by Cu, Fe, Mo, V, Ti or Pb.

C. D. Kopkin

4168. **Colorimetric determination of chromium in uranium compounds.** O. A. Vita and L. R. Mullins, jun. (Goodyear Atomic Corp., Portsmouth, Ohio, U.S.A.). *U.S. Atomic Energy Comm.*, Rep. GAT-T-843, 1960. 7 pp.—A method for the rapid micro-determination of Cr was developed. The Cr is oxidised to Cr^{VI} with permanganate and the excess of permanganate is reduced with bromide. The Cr is then determined by developing and measuring the colour of the Cr - diphenylcarbazide complex. This combination of oxidant and reductant gives the method advantages over similar methods published, namely, excess of reductant can be used without close control and a stable Cr - diphenylcarbazide complex is formed. Amounts of 1 to 10 μg of Cr can be determined with a 10% limit of error at the 95% confidence level.

Nucl. Sci. Abstr.

4169. **Determination of trace amounts of chromium in uranium.** A. Huart (Centre d'Études Nucl., Saclay, France). *Rapp. Cent. Étud. Nucl. Saclay*, No. 1230, 1959. 12 pp.—A method for the photometric determination of Cr in the presence of U by use of the extinction of the Cr^{VI} - diphenylcarbazide complex at 540 mμ involves oxidation, with $KMnO_4$, removal of the excess of oxidant, and formation of the complex. By careful control of conditions the method was suitable for the determination of 0·5 to 15 p.p.m. of Cr in uranium metal.

Chem. Abstr.

4170. **Determination of the stoicheiometry of uranium dioxide by controlled-potential coulometry.** R. W. Stromatt and R. E. Connally (General Electric Co., Richland, Wash., U.S.A.). *Anal. Chem.*, 1961, **33** (3), 345–346.—The ratio (*A*) of

O to U in uranium oxides can be determined in $\simeq$ 40 min. by controlled-potential coulometric titration of total U and of U^{6+} in dil. H_2SO_4 soln. after dissolution of the finely ground sample in hot conc. H_3PO_4 (O-free) in the presence of He. The correct integrator range is selected, the sample-aliquot is pre-reduced at + 0·05 V *vs.* the S.C.E., and then reduced at − 0·38 V to obtain the concn. of total U. A twofold excess of $Ce(SO_4)_2$ is then added to form U^{6+}, and the soln. is pre-reduced and reduced as before. A is calculated from the equation $A = 2{\cdot}0 + U^{6+}/U$. The accuracy is $\simeq$ 0·1% when A is $\lesssim$ 2·1, and $\simeq$ 1% when A is 2·1 to 2·01; the standard deviation for reproducibility is $\pm$ 0·0003 to $\pm$ 0·0009 (33 analyses). The value of A for freshly reduced UO_2 is 2·0003 and for U_3O_8 is 2·6677. W. J. BAKER

4171. **Null-point potentiometric determination of fluoride.** T. A. O'Donnell and D. F. Stewart (Dept. of Chem., Univ. of Melbourne, Victoria, Australia). *Anal. Chem.*, 1961, **33** (3), 337–341.—The procedure is based on the complexing of Ce^{IV} with F^- and the resulting lowering of the Ce^{IV} - Ce^{III} redox potential. The sample soln. is added to one Ce^{IV} - Ce^{III} half-cell and 0·05M-NaF is added to a similar half-cell until the p.d. is zero. The electrolyte used is 0·01M-Ce^{3+} - 0·01M-Ce^{4+} - 0·25M-H_2SO_4; during the titration the acidity and ionic strengths must be kept the same in each half-cell. For concn. of F^- from 0·05 to 0·5M the error is $\simeq$ 0·2%; for 5×10^{-3} to 10^{-2}M the concn. of all reagents must be scaled down so that the optimum ratio (2:1:1) of F^-:Ce^{4+}:Ce^{3+} is maintained, the error in this range being 0·5 to 1%. There is no significant interference from Cl^- (in amount equiv. to F^-), SO_4^{2-}, NO_3^-, Na, K, NH_4^+, Co or Ni, but the effects of acetate, oxalate, PO_4^{3-}, MoO_3^- and U or high concn. of Cl^- must be avoided by a compensation procedure or otherwise. The applications of the method to binary and complex fluorides (including dental fluxes), ion-exchange eluates, Willard - Winter distillates, and soln. from pyrohydrolysis are described. W. J. BAKER

4172. **Application of stripping analysis to the determination of iodide with silver micro-electrodes.** I. Shain and S. P. Perone (Univ. of Wisconsin, Madison, U.S.A.). *Anal. Chem.*, 1961, **33** (3), 325–329.—A pre-treated silver micro-electrode is immersed in an aliquot of the sample soln. and is oxidised at constant potential under controlled conditions such that a fraction of the AgI is formed readily without significant amounts of free silver. The deposit is then stripped cathodically, either by electrolysis at constant potential or by voltammetry at linearly varying potential. The concn. of AgI is calculated from the pre-electrolysis time and the amount of electricity used in stripping. The accuracy is within $\simeq$ 1% for concn. of 4×10^{-4} to 10^{-6}M and the sensitivity is 4×10^{-8}M. Interferences and optimum operating conditions are discussed. W. J. BAKER

4173. **Spectrophotometric determination of technetium with toluene-3,4-dithiol.** F. J. Miller and P. F. Thomason (Oak Ridge Nat. Lab., Tenn., U.S.A.). *Anal. Chem.*, 1961, **33** (3), 404–406.—Microgram amounts of Tc can be determined by measuring the extinction of its coloured complex with toluene-3,4-dithiol in aq. 2·5N-HCl after extraction into CCl_4. One hour must be allowed for the development of the colour, the intensity of which is max. at 450 mμ (molar absorptivity 1·5 $\times$ 10^3). Beer's law is followed over the range of 1·5 to 16·5 μg of Tc per ml; the error is $\gtrsim \pm$ 5%. Because many cations interfere, an initial separation of Tc is necessary (*cf.* Boyd, *J. Chem. Educ.*, 1959, **36**, 39; Clark and Neville, *Ibid.*, 1959, **36**, 390). W. J. BAKER

4174. **Effect of nitric acid on the extraction of iron with tri-n-octylphosphine oxide.** J. O. Hibbits, W. F. Davis and M. R. Menke (General Electric Co., Cincinnati, Ohio, U.S.A.). *Talanta*, 1961, **8** (2–3), 164–165 (in English).—Nitric acid interferes with the extraction of Fe from soln. in HCl. R. M. ROWLEY

4175. **Determination of iron with 1,10-phenanthroline.** J. O. Hibbits, W. F. Davis and M. R. Menke (General Electric Co., Cincinnati, Ohio, U.S.A.). *Talanta*, 1961, **8** (2–3), 163–164 (in English).—*Procedure*—To a soln. containing $\simeq$ 100 μg of Fe add M-HCl (20 ml), 4% Na acetate soln. (5 ml), 10% hydroxyammonium chloride soln. (2 ml) and citric acid (1 g). Adjust the pH to 4·0 $\pm$ 0·1 with NaOH soln., add 0·3% 1,10-phenanthroline soln. (15 ml), and make up the volume to 100 ml. Allow the soln. to stand overnight, then measure the extinction at 510 mμ. When this procedure is used, Cr, Co, Ni, Rh and Pd interfere at the 10-mg level, but not at the 1-mg level. Other elements do not interfere. R. M. ROWLEY

4176. **Complexometric determination of iron.** I. P. Alimarin and Yün-Hsiang Tsê (School Anal. Chem., Moscow Univ.). *Vestn. Moskov. Univ., Ser. Khim.*, 1961, (1), 59–63.—*N*-Benzoyl-*N*-phenylhydroxylamine (0·5% in acetone), *N*-phenylhydroxamic acid (3% aq.) and *N*-(sulphophenyl)-hydroxamic acid (3% aq.) form red - violet complexes with Fe^{3+} at pH 1 to 1·5, which can be used as indicators in EDTA titrations. *Procedure*—Dissolve the sample in acid, neutralise the soln. with aq. NH_3 (1:4) to the appearance of a turbidity, add 10 ml of N-HCl, dilute to 100 ml and heat to 50° to 60°. Add 1 to 2 ml of indicator and titrate with 0·02M- or 0·05M-EDTA to a lemon-yellow colour. Titanium, Zn and Th interfere, but rare-earth metals, Al and small amounts of Co^{2+}, Ni^{2+} and Cu^{2+} do not. J. W. PRICE

4177. **Use of electrolytically generated chlorine for the coulometric determination of ferrous iron.** V. K. Khakimova and P. K. Agasyan (M. V. Lomonosov Moscow State Univ.). *Zavod. Lab.*, 1961, **27** (3), 263–266.—The anode compartment contains the soln. of Fe ($\lesssim$ 10 μg) in 5M-HCl and the cathode compartment, connected with the anode compartment by means of a salt bridge, contains 5M-HCl alone. Generation of Cl is carried out intermittently, with intervals of about 2 sec. near the end-point, which is determined potentiometrically. G. S. SMITH

4178. **Quantitative estimation of ferric iron by arsenic acid in aqueous alcoholic medium.** T. Chandra Gupta and A. K. Bhattacharya (Chem. Dept., Agra College, India). *Z. anal. Chem.*, 1961, **180** (1), 37–38 (in English).—The complexes of $FeCl_3$ with arsenic acid are reduced sufficiently in solubility for titration purposes by the addition of ethanol or acetone. *Procedure*—Mix 0·1M-arsenic acid (10 ml) and ethanol (10 ml). Titrate with 0·066M to 0·2M-$FeCl_3$ with 5% aq. cupferron (0·5 ml) or satd. $K_4Fe(CN)_6$ (0·3 ml) as external indicator.

Results are 2% low and a correction factor may be applied. Iron ores may be dissolved in HCl and titrated directly. G. RUSSELL

4179. Determination of iron in aluminium salts. F. S. Frum, N. P. Polovinkina and S. V. Sheshulina. *Trudy Khim. i Khim. Tekhnol.* [*Gor'kii*], 1959, (3), 574–578; *Ref. Zhur., Khim.*, 1961, (1), Abstr. No. 1D114.—Two colorimetric methods are used, based on the reactions of Fe with NH_4SCN and sulphosalicylic acid, respectively. *Procedure with NH_4SCN*—Dissolve the sample (20 to 200 mg) in water (5 ml for the photometric determination, or 1 ml when using a standard scale corresponding to 0·1 to 1 μg of Fe per ml). To the soln. add 0·1 to 0·2 ml of HNO_3 (1:1) and 0·2 ml of a 15% NH_4SCN soln. followed by a mixture of ethyl ether and isoamyl alcohol (1:2) (7 ml), shake for 5 min., set aside for 10 min., and measure the extinction of the org. layer at 496 mμ in a 1-cm cell. The error is $\not>$ 10%. For the standard series method, 0·5 ml of the solvent mixture is sufficient; the error is $\not>$ 7%. *Procedure with sulphosalicylic acid*—To the test soln. add 2·0 ml of a 5% sulphosalicylic acid soln. and 0·5 ml of 10% aq. NH_3 and compare the resulting colour with that of the standard scale. For photometry, double the quantities used. The error is 6%. Both methods can be used to determine 10^{-4} to 10^{-5} % of Fe. C. D. KOPKIN

4180. Determination of niobium in cast iron. A. I. Ponomarev and A. Ya. Sheskol'skaya. *Trudy Inst. Metallurg., Akad. Nauk SSSR*, 1960, (4), 240–242; *Ref. Zhur., Khim.*, 1961, (1), Abstr. No. 1D98.—A tannin method, without preliminary removal of Fe and Ti, is suggested for the determination of Nb in cast iron. *Procedure*—Dissolve the sample (1 to 1·5 g) on a sand bath in 5 ml of HNO_3 (sp. gr. 1·40), evaporate the soln. almost to dryness, add 30 ml of HCl (1:2) and boil till the sample is completely dissolved, maintaining the volume by adding water (a black residue of C may remain). Dilute the soln. to 180 or 190 ml, add 0·1 to 0·2 g of ascorbic acid to complex Ti and reduce Fe, heat to between 70° and 80°, precipitate Nb by adding 10 ml of freshly prepared 1% aq. tannin soln. slowly and with stirring, and maintain at this temp. for 2 to 3 hr. After cooling and complete coagulation, filter off the ppt. with filter-paper pulp on paper and wash it (× 6 or 8) with cold 4% HCl. Ignite the ppt. and filter in a platinum crucible, add water, 10 to 20 drops of H_2SO_4 (1:1) and 2 to 3 ml of HF, evaporate to fumes, and re-precipitate the Nb. Ignite the Nb_2O_5 ppt. at 1000°, weigh it, fuse it with 0·5 to 1·0 g of $K_2S_2O_7$, dissolve the melt in 20 ml of 5% H_2SO_4, add 1 or 2 drops of H_2O_2, determine the co-pptd. Ti colorimetrically, and apply a correction. C. D. KOPKIN

4181. Direct absorptiometric determination of copper in steel and cast iron with 2,2′-biquinolyl. C. E. A. Shanahan and R. H. Jenkins (Central Res. Lab., Richard Thomas & Baldwins Ltd., Whitchurch, Bucks., England). *Analyst*, 1961, **86**, 166–171.—The sample (0·5 g) is dissolved in HCl and the soln. is evaporated to dryness after addition of HNO_3 and again after moistening with HCl. The baked residue is warmed with HCl and diluted to 100 ml. To a 10-ml aliquot are added 5 ml of 20% aq. ascorbic acid soln. and, after mixing, 25 ml of 0·06% 2,2′-biquinolyl soln. (0·06% w/v in dimethylformamide) and the mixture is diluted to 50 m l at 20°. A second 10-ml aliquot is treated with ascorbic acid and dimethylformamide and diluted similarly. The extinction of the test soln. is measured against the compensating soln. The result of a blank determination obtained with a sample of pure iron subjected to the procedure is deducted, and the final figure is referred to a calibration graph. Quoted results indicate satisfactory precision. A. O. JONES

4182. Differentiated phase analysis of complex alloy steel of the type ÉI 481. K. P. Sorokina. *Zavod. Lab.*, 1961, **27** (3), 253–256.—Preliminary anodic dissolution is carried out at a c.d. of 0·05 amp. per sq. cm in HCl - methanol soln. Boiling with HCl - H_2O_2 soln. then serves to separate chromium carbide ($Cr_{23}C_6$), and boiling with HNO_3 serves to separate VC and NbC. G. S. SMITH

4183. Coulometric determination of ferrocyanides. V. Kulandaivelu and A. P. Madhavan Nair (Alagappa Chettiar Coll. of Technol., Univ. Madras, India). *Z. anal. Chem.*, 1961, **179** (5), 342–344 (in English).—The method is an extension of those previously developed for thiocyanate (Nair and Ibrahim, *J. Sci., Ind. Res., India*, 1956, **15**, 703) and ferricyanides (Santhanam and Nair, *Z. anal. Chem.*, 1959, **169**, 102), with a silver anode. *Procedure*—Prepare a buffer of pH 5 [0·2M-acetic acid - 0·2M-Na acetate (1:3)] and de-oxygenate an aliquot by passing H for 15 min. Remove reducible impurities from the buffer by electrolysis, then add the $[Fe(CN)_6]^{4-}$ soln. (total vol. $\simeq$ 100 ml). Electrolyse at + 0·32 V *vs.* the S.C.E. till the current falls to < 1 mA. Collect the H - O mixture in the coulometer and calculate the $[Fe(CN)_6]^{4-}$ from the vol.; 30 to 40-mg amounts of $K_4Fe(CN)_6.3H_2O$ require about 1 hr. for coulometry with the apparatus used. The mean error for 30 to 70 mg of $[Fe(CN)_6]^{4-}$ (8 determinations) was $\pm$ 0·6%. Positive errors were obtained in the presence of Cl^-; with Cl^- equiv. to 1·2% of the wt. of $[Fe(CN)_6]^{4-}$, the error was + 2·1%. G. RUSSELL

4184. Catalytic analysis. II. Detection of sub-micro amounts of cobalt by the tiron - orcinol - hydrogen peroxide redox system. J. Bognár and O. Jellinek (Tech. Univ., Miskolc, Hungary). *Magyar Kém. Foly.*, 1961, **67** (3), 100–103.—By this method 10^{-5} μg of Co^{2+} can be detected in 5 ml of soln. The speed of the reaction is influenced by the concn. of reagent, concn. of oxidant, temp. and pH (max. at 10·8). The H_2O_2 can be replaced by sodium perborate; 5×10^{-5} μg of Co^{2+} can then be detected in 5 ml of soln. The interfering effects of elements and compounds were investigated. Lead, Hg, Bi, As, Sb, K, Na, Ca, Pt, Se, Te, Tl and W do not interfere; Fe, Mo, C, Cu Ti and V interfere by formation of coloured complexes; Mn, Ni and OsO_4 interfere by catalytic action. 1-Nitroso-2-naphthol, 1-nitroso-R salt, 2,2′-bipyridyl, 1,10-phenanthroline, 8-hydroxyquinoline, ammonia, dimethylglyoxime, EDTA, KCN and CO_2 gas act as catalytic poisons. The strong catalytic action of Co in the catechol - orcinol - H_2O_2 system can also be used. In this case 10^{-4} μg of Co^{2+} can be detected in 5 ml of soln., but this reaction is much more dependent on environmental factors. The Co^{2+} have no catalytic effect in the resorcinol - H_2O_2 or tiron - resorcinol - H_2O_2 systems.

III. Detection of sub-micro amounts of cobalt by the tiron - apomorphine - hydrogen peroxide reaction. J. Bognár and O. Jellinek. *Ibid.*, 1961, **67** (3), 103–106.—The oxidation of apomorphine

by H_2O_2 in the presence of the Co - tiron complex is described. By this reaction 5×10^{-5} μg of Co^{2+} can be detected in 5 ml of soln. *Procedure*—The test soln. (1 ml), tiron soln. (0·5% in 50% ethanol) (1 ml), apomorphine soln. (0·5% of the hydrochloride in 50% ethanol) (1 ml), H_2BO_3 buffer soln. (0·4 g of H_3BO_3 in 100 ml of 0·1N-NaOH) (0·5 ml) and H_2O (0·5 ml) are mixed in a test-tube. A blank soln. is also prepared and each soln. is made up to 5 ml with 0·3% H_2O_2 soln. The soln. containing the Co becomes pink in a few minutes, while the development of colour in the blank soln. is much slower. A Pulfrich photometer was used to follow the reaction. The rate of reaction is affected by pH (max. between 9·5 and 10·5), concn. of reagents and temp. The effects of 35 elements on the reaction are tabulated. Complex-forming materials, *e.g.*, 1-nitroso-2-naphthol, pyridine and EDTA, act as catalytic poisons.

B. VASZKO

4185. **Determination of cobalt in heat-resistant alloys.** H. Kirtchik and F. H. Swearingen (Flight Propulsion Lab. Dept., General Electric Co., Evendale, Ohio, U.S.A.). *Analyst*, 1961, **86**, 188–195.—A soln. of the sample in HCl and HNO_3 is treated with H_3PO_4, dil. H_2SO_4 and $HClO_4$, and most of the $HClO_4$ is removed by evaporation. The residue is boiled with water, ammonium citrate is added to the diluted soln., the pH is adjusted to 8 with aq. NH_3 and an excess (10 ml) is added. After diluting and cooling the soln. to $\simeq 35°$, the Co is selectively pptd. by a combination of 4-phenyl-3-thiohydantoic and thioglycollic acids. The collected ppt., with the filter-paper, is freed from organic matter by heating with HNO_3 and $HClO_4$, the residue is dissolved in water and the soln. is titrated potentiometrically in the presence of ethylenediamine, a measured excess of $K_3Fe(CN)_6$ soln. [standardised against $Co(NO_3)_2$] being added and the mixture back-titrated with $Co(NO_3)_2$ soln. With alloys containing $> 3\%$ of Co, errors of $< 4\%$ can be expected.

A. O. JONES

4186. **Conditions for the precipitation of nickel with dimethylglyoxime in the presence of cobalt.** M. V. Korotun. *Ukr. Khim. Zhur.*, 1960, **26** (3), 377–380; *Ref. Zhur., Khim.*, 1961, (1), Abstr. No. 1D116.—In the pptn. of Ni with dimethylglyoxime (**I**) in the presence of Co, the order of reaction of **I** with Ni and Co, *i.e.*, the relative rates of formation of the ppt. (depending on the pptn. conditions), is of importance for obtaining pure nickel dimethylglyoxime (**II**). In acetic acid medium, Co^{2+} react with **I** progressively, increase of the concn. of **I** increasing the rate of reaction, so that the ppt. of **II** may be contaminated with Co. In weakly acid medium Ni must therefore be pptd. with the minimum excess of **I** in the presence of Co. In ammoniacal soln. Ni reacts with **I** only after Co^{2+} have been completely complexed. If Co^{2+} are oxidised to Co^{3+}, Ni is then the first to react with **I** in ammoniacal medium. The pptd. **II** reacts only very slightly with the cobaltammine during 3 to 5 hr. A disadvantage of this method is that the ppt. of **II** is contaminated with cobalt hydroxide; this can be removed by re-pptn. To determine Ni in cobalt salts, dissolve the sample (2 g) in the minimum of water, add 10 to 12 g of $(NH_4)_2SO_4$, 7 to 8 ml of 20% aq. NH_3 and 2 g of $(NH_4)_2S_2O_8$. Carry out the oxidation first in the cold and then boil the soln. Cool, acidify with dil. HCl (if a ppt. forms add water until it dissolves), add 10 to 15 ml of 1% ethanolic **I** soln., and satd. Na acetate soln. until the pH is 5. After 1 to 1·5 hr. filter off the **II** and re-precipitate it.

C. D. KOPKIN

4187. **Volumetric determination of cobalt and nickel in hard magnetic alloys.** R. D. DeMars (IBM Res. Center, Yorktown Heights, N.Y., U.S.A.). *Anal. Chem.*, 1961, **33** (3), 342–344.—Small amounts of Ni and Co can be determined rapidly and simultaneously by voltammetry with continuously varying potential, at the dropping-mercury electrode, in a 0·2M-pyridine - 0·2M-KCl electrolyte at pH 6. The peak potentials are −0·81 V for Ni and −1·10 V for Co (both *vs.* the S.C.E.). The current *vs.* voltage curves are obtained with an instrument based on an analogue-computer amplifier, and are then referred to standard curves. For concn. of each element in the range of 10^{-3} to 10^{-5}M (≡ 1 to 12 mg per 200 ml) the error is from 0·01 to 1 mg; the accuracy is less for concn. of 10^{-4} to 10^{-6}M. A tenfold excess of Cu can be tolerated.

W. J. BAKER

4188. **Phase analysis of nickel - beryllium alloys.** N. I. Blok, N. F. Lashko and O. A. Khromova. *Zavod. Lab.*, 1961, **27** (3), 251–252.—Electrolysis of nickel alloys containing 1·93% of Be, 2·20% of Be and 5·0% of Mo, and 2·66% of Be and 1·18% of W, respectively, and aged at various temperatures was carried out at a c.d. of 0·06 amp. per sq. cm in an electrolyte containing 10 g of trisodium citrate in 1200 ml of 12% aq. NH_3, and the phase distribution of Be was determined.

G. S. SMITH

4189. **Absolute determination by X-ray diffraction of a binary or ternary mixture: nickel oxide and fluoride in nickel powder.** P. Charpin and A. Hauptman (Centre d'Études Nucl., Saclay, France). *Rapp. Cent. Étud. Nucl. Saclay*, No. 1549, 1960. 12 pp.—The method employed is based on the comparison between computed and measured intensities for conveniently selected X-ray diffraction lines of each component of the powder. Care must be taken to allow for absorption, both inside each grain and in the over-all sample. This method was applied to the determination of nickel oxide and fluoride in nickel powder.

NUCL. SCI. ABSTR.

4190. **Spectrographic analysis of solutions containing metals of the platinum group.** N. A. Sin'kov. "Spektr. Anal. v Tsvet. Metall.", M., Metallurgizdat., 1960, 326–331; *Ref. Zhur., Khim.*, 1961, (1), Abstr. No. 1D117.—The platinum-group metals are pptd. from soln. by cementation with zinc dust. Take a sample of soln. containing 0·2 to 2 mg of metals, add 10 ml of 2% $CuSO_4$ soln., dilute to 200 to 500 ml and heat the soln. to 80°. With constant stirring add 5 to 8 g of zinc dust in 200 to 300-mg portions, adding each portion after the previous one has dissolved. After the soln. is decolorised, continue the cementation for 5 to 10 min., then filter on a Büchner funnel with suction. Wash the ppt. with hot water acidified with HCl, to remove salts of non-noble metals, dry the residue and fuse it with copper to obtain a regulus of $\simeq 2$ g. Use two halves of the regulus as electrodes in an a.c. arc, and photograph the spectra in a medium quartz spectrograph. Construct a calibration curve. Copper is used as comparison element; 0·005 to 0·1% of Pt, Ir, Au, Rh, Ru or Pd can be determined; the error is ± 10 to 15%. For higher concn., place the soln. in a hollow porous graphite electrode with a bottom thickness of 1 mm; ignite a spark between this electrode and a lower graphite electrode sharpened to an angle of 45°. The generator has

zero self-induction, capacity 0·01 μF and current 2 amp. Platinum, Rh and Pd can be determined with errors of $\pm$ 2·5 to 9·2%. C. D. KOPKIN

4191. **Spectrophotometric determination of palladium(II) with 5-(*p*-dimethylaminobenzylidene)-rhodanine.** G. H. Ayres and B. D. Narang (Dept. of Chem., Univ. of Texas, Austin, U.S.A.). *Anal. Chim. Acta*, 1961, **24** (3), 241–249 (in English).—5-(*p*-Dimethylaminobenzylidene)rhodanine (**I**) reacts with Pd^{2+} in a mol. ratio of 2:1; the influence of formic and propionic acids, and of HCl and various cations is discussed. A small excess of Pt^{4+}, Ru^{3+}, Ir^{3+}, Fe^{3+}, Cr^{6+} and Cu^{2+} may be present; Au^{3+} interfere. *Procedure*—To 3 ml of 0·1N-HCl, containing 5 to 25 μg of Pd^{2+}, add 3 ml of 88% formic acid soln. and 1 ml of reagent (0·04% of **I** in 44% formic acid) and dilute to 10 ml with H_2O. After 7 to 10 min. measure the extinction at 515 mμ against a reagent blank; Beer's law is followed up to 2·5 p.p.m. of Pd.

P. D. PARR-RICHARD

4192. **Colorimetric procedure for checking the palladium content of jewellery alloys.** R. W. Johnson (The Mond Nickel Co. Ltd., Devel. and Res. Dept., Platinum Metals Div., Bashley Rd., London). *Analyst*, 1961, **86**, 185–188.—The soln. of the alloy ($\equiv \simeq$ 15 mg of Pd) in aqua regia is evaporated and the residue is dissolved in N-HCl (15 ml). If necessary the soln. is filtered (to remove AgCl, H_2MoO_4 and H_2WO_4) and treated with 15 ml of 20% $FeSO_4$ soln. and the calculated vol. of 0·01N-KI to give a small residual trace of unpptd. Pd. The well-shaken soln. is set aside for $\simeq$ 15 min. and a portion is centrifuged. An aliquot of the supernatant liquid is treated with 5 ml of a buffer soln. (48 ml of N-HCl and 132 ml of N-Na acetate diluted to 200 ml) and 0·25 ml of *p*-nitrosodimethylaniline soln. (0·25% in 50% aq. ethanol). The colour is compared with that of a standard prepared similarly from 0·4 ml of standard Pd soln. (5 p.p.m.). If the colour of the sample soln. is more intense than that of the standard the Pd content of the sample is not less than nominal. The method would be suitable as a "pass or fail" test if the recently discussed hall-marking of palladium alloys is adopted. A. O. JONES

4193. **Spectrophotometric determination of microgram quantities of osmium with diphenylcarbazide.** G. Goldstein (Oak Ridge Nat. Lab., Tenn., U.S.A.). *U.S. Atomic Energy Comm.*, Rep. CF–59–7–16, 1959. 2 pp.—A method was developed for the determination of 30 to 100 μg of Os. The Os as OsO_4 is extracted with $CHCl_3$ and diphenylcarbazide is added to the organic extract. A blue-violet product is formed the extinction of which is measured at 560 mμ. A suitable reagent concn. is from 3 to 5 ml of 0·2% diphenylcarbazide soln. in a vol. of 25 ml and the preferred solvent for the reagent is ethanol. Beer's law is followed over a range of 8 to 130 μg of Os, with a coeff. of variation of about 4%. After a 2-hr. colour-development period, the molar extinction coeff. is 31,300. Attempts to achieve reproducible measurements of extinction in less than 2 hr. were unsuccessful. Only Ru^{VIII} interfered.

NUCL. SCI. ABSTR.

4194. **Determination of traces of osmium and iridium in samples of palladium and platinum by neutron-activation analysis.** D. F. C. Morris and R. A. Killick (Dept. of Chem., Brunel Coll. of Technol., Acton, London, England). *Talanta*, 1961, **8** (2–3), 129–137 (in English).—Samples and standards containing added Os and Ir were sealed in silica tubes and irradiated at A.E.R.E. Harwell. The samples of palladium were irradiated in Pile BEPO for 1 week with a thermal neutron flux of 10^{12} per sq. cm per sec.; the samples of platinum were irradiated in Pile DIDO for 1 week with a neutron flux of 9×10^{11} per sq. cm per sec. After irradiation, known amounts of Os and Ir were added to the samples as carriers. Osmium was separated by distillation of OsO_4, and purified by pptn. as hydrated OsO_2 and reduction by H to the metal; Ir was separated from Pd and Pt by pptn. of these with HgCl in the presence of Br^-, and purified by pptn. as hydrated IrO_2 and reduction to the metal. The activity of the separated Os was measured with an end-window Geiger-Müller counter, and that of the Ir with a γ-scintillation counter. Samples of platinum in which no Os or Ir could be detected by spectrographic analysis were found to contain 0·03 to 0·96 p.p.m. of Os and 0·10 to 3·37 p.p.m. of Ir. A sample of palladium was found to contain 0·08 p.p.m. of Os and 10·8 p.p.m. of Ir. R. M. ROWLEY

4195. **Ultra-violet spectrophotometric determination of osmium tetroxide in chloroform.** G. Goldstein (Oak Ridge Nat. Lab., Tenn., U.S.A.). *U.S. Atomic Energy Comm.*, Rep. CF–59–6–43, 1959. 9 pp.—The Os is first oxidised to Os^{VIII} and the OsO_4 formed is extracted selectively with $CHCl_3$. The u.v. absorption spectrum of OsO_4 in $CHCl_3$ has a series of absorption bands with peaks at 282, 289, 297, 304 and 312 mμ and molar extinction coeff. of 1870, 1760, 1640, 1400 and 1000, respectively. For each wavelength the optimum concn. range for the determination of Os was evaluated by the method of Ringbom. Only Cl^- and Ru^{VIII} interfere. By this method, 0·4 to 3 mg of Os can be determined with a coefficient of variation of 3%.

NUCL. SCI. ABSTR.

4196. **Fully automatic measurement of the moisture content of sands and ceramic bodies. II. Determination of the moisture content of sand by absorption in the micro-wave band.** E. M. Amrhein (Max-Planck Inst. Silikatforsch, Würzburg, Germany). *Ber. dtsch. keram. Ges.*, 1960, **37** (12), 520–523.—The measurement is based on the max. absorption band of H_2O at 30×10^9 c/s. The plane polarised radiation (from a klystron generator), which is transmitted through a standard bed of sand, is measured. A calibration curve relating moisture content with extinction is linear over the range 0 to 3% of H_2O. If care is taken with the mechanical stability and constancy of the valve characteristics and supply voltage, an accuracy of $\pm$ 0·2% by wt. is possible. The apparatus (some details of which are recorded) was adapted to give a continuous reading for sand being conveyed around a circular track of Plexiglas (used on account of its isotropic nature). A change of 0·25% of H_2O content was clearly recorded on a chart. J. A. SUGDEN

4197. **Rapid methods of analysis of clay, kaolin and talc.** I. M. Yurist and O. I. Korotkova. *Zavod. Lab.*, 1961, **27** (3), 274–277.—The sample (0·5 g) is placed on 2·5 to 3 g of $KHSO_4$, covered with 2·5 g of $KHSO_4$ and fused at 800° until evolution of SO_3 ceases. The cooled melt is heated with dil. H_2SO_4 and filtered. The SiO_2 is determined in the usual way. The filtrate is diluted to 250 ml. For determining Fe, Al and Ti, an aliquot (20 ml)

is treated with 2 or 3 drops of 30% H_2O_2 soln. and neutralised to Congo red paper with N-NaOH, followed by the addition of 5 ml of N-HCl and 0·5 ml of 20% sulphosalicylic acid soln. After dilution to ≃ 100 ml, the soln. at 70° is titrated for Fe with 0·01M-EDTA. The titrated soln. is then treated with more EDTA soln. (10 ml of 0·05M for clay and kaolin and 5 ml of 0·01M for talc)and neutralised with 10% ammonium acetate soln. (violet colour with Congo red paper) followed by addition of 20 ml of a buffer soln. (54 g of cryst. Na acetate dissolved in 100 ml of water and mixed with 100 ml of 2N-acetic acid) and 1 ml of 20% sulphosalicylic acid soln., and dilution to 300 ml. The soln. at 75° to 80° is titrated for the sum of Al and Ti with $FeCl_3$ soln. to the transition from greenish-yellow to orange. A separate colorimetric determination of Ti with H_2O_2 is carried out and the content of Al is obtained by difference. For determining Ca and Mg, a second aliquot (20 ml) is neutralised with 2N-NaOH in the presence of 1 drop of 0·01% methyl red soln., then treated with 5 ml of 2N-NaOH and diluted to ≃ 100 ml, and titrated for Ca with 0·01M-EDTA in the presence of 10 drops of Acid Chrome dark blue (C.I. Mordant Blue 7) soln. (0·25 g dissolved in a mixture of 50 ml of ethanol and 5 ml of an ammoniacal buffer soln.). The titrated soln. is mixed with 5 ml of 50% tartaric acid soln. (to dissolve the hydroxides and to mask the effect of Al, Ti and Fe) and treated with 25% aq. NH_3 until a slight odour of NH_3 remains, followed by addition of 10 ml of a buffer soln. (20 g of NH_4Cl and 80 ml of aq. NH_3 per litre) and titration for Mg with EDTA soln. (0·05M for talc and 0·01M for materials with lower concn. of Mg). G. S. SMITH

4198. **Polarographic methods for the analysis of acid gold alloy plating solutions.** A. H. Craft and K. Schumpelt (Sel-Rex Corp., Nutley, N.J., U.S.A.). *Plating*, 1961, **48** (3), 277–279.—Plating soln. containing Au, Co, Ni and In are fumed with H_2SO_4 to destroy organic matter and precipitate Au. Indium if present is pptd. as hydroxide and determined polarographically, and the filtrate is polarographed to determine Co and Ni. *Procedure*—To 2 ml of sample add 1 ml of conc. H_2SO_4 (and HNO_3 if organic matter is present) and evaporate to fuming. Cool, dilute, and precipitate In by adding dil. aq. NH_3 dropwise to the bromothymol blue end-point. Filter off the Au and $In(OH)_3$ and dissolve the In from the filter with 8·5 ml of HCl (1:1), washing the filter with H_2O; add 5 drops of 2% Triton soln., dilute to 50 ml, de-aerate with N, and polarograph: the In wave occurs at −0·65 V. Weigh the Au after ignition of the filter in a platinum crucible. To the first filtrate, containing Co and Ni, add 20 ml of aq. NH_3 - NH_4Cl (325 ml of conc. aq. NH_3 and 267·5 g of NH_4Cl in 2 litres of H_2O) and 15 drops of 0·2% Triton soln. and dilute to 50 ml. De-aerate with N and polarograph: the Co and Ni waves occur at −1·08 V and −1·3 V, respectively. Comparative results for Co, Ni and In determined by this method and by a standard (electrolytic) method are given; results by the standard method were difficult to reproduce for small amounts. C. S. HOWES

See also Abstracts—**4199**, Titration of weak acids. **4220**, Determination of hydroxylamine and hydrazine. **4277**, Cm in urine. **4278**, Ge in biol. materials. **4345**, Detection of Hg and Ag. **4412**, Anion exchange in non-aq. solvents. **4413**, Ion exchange with ethanol - HCl - water eluents.

3.—ORGANIC ANALYSIS

Determination of elements and radicals and of organic compounds not included in other sections. Organic industrial products, including petroleum and its products, fuels, detergents, volatile oils, cosmetics, dyestuffs, fibres, plastics, resins, paints, elastomers, leather and explosives.

4199. **Spectrophotometric titration of weak acids or bases in aqueous solution using the Type II plot.** S. Bruckenstein and D. C. Nelson (School of Chem., Univ. of Minnesota, Minneapolis 14, U.S.A.). *Anal. Chem.*, 1961, **33** (3), 438–444.—The Type II plot of Higuchi *et al.* (*Ibid.*, 1956, **28**, 1506) for the spectrophotometric titration of weak acids and bases is discussed for aqueous solutions. The range of application is given, together with details of the experimental procedure and actual titrations. It was found that acids or bases with a $pK \geqslant 9{\cdot}0$ can be determined with an accuracy of 0·2% in 0·1M concentration, and 0·07M-Na_2CO_3 can be titrated to bicarbonate with a similar accuracy. The method described is no lengthier than other photometric titrations, and can be used to determine the end-point of weaker acids and bases than by the more conventional methods of end-point detection. R. A. HENDEY

4200. **Micro-determination of carbon in organic compounds by the flask combustion procedure.** F. W. Cheng and C. F. Smullin (Chemical Res. Dept., Atlas Powder Co., Wilmington, Delaware, U.S.A.). *Microchem. J.*, 1961, **5** (1), 43–51.—The modified combustion flask, adapted for the determination of C in organic compounds (*Ibid.*, 1960, **4**, 213; 1961, **8**, 605), was used. The sample was ignited electrically and the CO_2 produced was absorbed, in the closed system, by an alkaline $BaCl_2$ soln. containing KCl. After the alkalinity of the soln. had been reduced, the pptd. $BaCO_3$ was filtered off, washed, and dissolved in an excess of 0·2N-HCl and the unchanged acid was back-titrated with 0·02N-KOH. In 11 analyses of benzoic acid, a mean carbon content was found of 68·82% ± 0·11 (theoretical 68·85%). The values determined for C in samples of representative compounds that contained N, S and halogen agreed with the calculated values to within 0·3% (relative). I. A. SIMPSON

4201. **Quantitative determination of carbon and hydrogen in organic compounds on a semi-micro scale.** C. Meyer and G. Vetter (Inst. Org. Chem., Tech. Hochsch., Dresden). *Chem. Tech., Berlin*, 1961, **13** (2), 104–109.—A full description is given of a rapid (30 min.) semi-micro combustion method and apparatus. *Procedure*—The sample (10 to 12 mg) is burnt in contact with a Co_3O_4 catalyst at 650° in a combustion tube in a controlled stream of dry O, and the combustion gases are passed first through an auxiliary heater (at 105°) to prevent condensation of water, and then successively over (*a*) Anhydrone, to absorb the water of combustion, (*b*) pptd. MnO_2 (specially prepared), to remove oxides of N and (*c*) soda asbestos, to absorb the CO_2. H. L. WHITEHEAD

4202. **Micro-determination of deuterium in organic substances.** J. Horáček (Inst. of Org. Chem., Czech. Acad. Sci., Prague). *Coll. Czech. Chem. Commun.*, 1961, **26** (3), 772–780 (in German).—The catalytic rapid-combustion method (with the

decomposition product of $AgMnO_4$ at 500°) yields water suitable without further purification for densimetric isotope analysis by the falling-drop method (Kestner *et al.*, *J. Biol. Chem.*, 1937, **122**, 227). For this determination, 0·1 to 0·2 ml of water suffices: the ^2H_2O - H_2O produced is diluted with standard water to this volume. Isobutyl benzoate is used as the medium for densimetry and 0·01 to 0·02% of ^2H_2O in the diluted material can be determined with high reproducibility. In routine analysis a single determination takes 60 to 90 min.

J. P. STERN

4203. **Modified method for the micro-determination of halogens in organic compounds.** W. A. Cook (Univ., Akron, Ohio, U.S.A.). *Microchem. J.*, 1961, **5** (1), 67–71.—*Procedure*—A weighed amount of the sample [≡ 7 to 10 ml of standard $Hg(NO_3)_2$ soln.] mixed with $Ba(NO_3)_2$ (4 to 6 mg) is burned in O in a Schöniger combustion flask (capacity 500 ml), charged with 2N-NaOH (10 ml). After complete absorption of the combustion products, the contents of the flask are treated as follows. For compounds containing Cl or Br, 2N-HNO_3 (1 ml), 0·2N-HNO_3 (4 ml) and 12 drops of diphenylcarbazone indicator soln. (1% in methanol) are added and the mixture is titrated, to a violet - blue end-point, with $Hg(NO_3)_2$ soln., previously standardised against 0·01N-NaCl. For compounds containing iodine, 0·02N-HNO_3 (1 ml), 0·2N-HNO_3 (5 ml) and 3 or 4 drops of hydrazine soln. (10%) are added, with gentle rotation of the flask to discharge the iodine colour. After the addition of 10% pyridine soln. (9 ml) and ensuring that the soln. is acid to litmus, 12 to 15 drops of diphenylcarbazone indicator soln. are added and the mixture is titrated to a deep-blue end-point with $Hg(NO_3)_2$ soln., previously standardised against 0·01N-KI. A titration blank is run in each case. The results of the analyses of 15 compounds, the halogen content of which varied from 12·28 to 96·69%, showed good agreement with theoretical values.

I. A. SIMPSON

4204. **Rapid micro-methods of elemental analysis. II. Determination of fluorine in organic compounds.** E. C. Olson and S. R. Shaw (The Upjohn Company, Kalamazoo, Mich., U.S.A.). *Microchem. J.*, 1961, **5** (1), 101–108.—The combination of a Schöniger oxygen flask combustion (*Anal. Abstr.*, 1955, **2**, 1816; 1957, **4**, 924) and the thorium chloranilate method of Hensley and Barney (*Anal. Abstr.*, 1961, **8**, 552) provides a rapid, sensitive and precise method for the determination of F in organic compounds. *Procedure*—The sample (containing 0·2 to 0·6 mg of F) is burnt in a quartz Schöniger oxygen flask (Pyrex-glass flasks give low results), and the combustion products, after complete absorption in H_2O, are transferred to a 100-ml flask containing ethanol - methanol - H_2O (18:1:1) (50 ml) and buffer soln. (10 ml of 90% formic acid and 4 g of NaOH, made up to 1 litre with de-ionised H_2O) (5 ml) and the soln. is diluted to vol. with the alcohol mixture and de-ionised H_2O (1:1). About half the contents of the flask is shaken for 75 ± 5 min. with thorium chloranilate (100 to 150 mg) and, after centrifuging a portion of the suspension at 2000 r.p.m. for 10 min., the extinction at 331 to 332 mμ of a dilution (1:5) of the supernatant liquid with de-ionised H_2O is measured, quartz absorption cells and a H_2O blank being used. The F^- content is calculated by use of a calibration curve. The results of 20 determinations on samples that varied in weight from 3·039 to 9·682 mg and in F content from 5·02 to 14·66% showed a standard deviation from the theoretical values of 0·113%.

I. A. SIMPSON

4205. **Micro-determination of fluorine (constituent or trace) in organic substances.** F. Martin, A. Floret and M. Dillier (Soc. Usine Chim. Rhône-Poulenc, Vitry-sur-Seine, France). *Bull. Soc. Chim. France*, 1961, (3), 460–467.—Two methods are described, *viz*, titration with $Th(NO_3)_4$, with Alizarin red S as indicator, and colorimetric determination by means of a Zr - alizarin sulphonate complex. The soln. of F^- are prepared by methods previously described (Martin and Floret, *Anal. Abstr.*, 1959, **6**, 197; 1960, **7**, 559). The first method is suitable for the determination of F in compounds and the second for F as a trace impurity down to 0·001%.

G. BURGER

4206. **The micro-Kjeldahl determination of nitrogen. An investigation of the effects of added salt and catalysts.** P. R. W. Baker (The Wellcome Res. Lab., Langley Court, Beckenham, Kent, England). *Talanta*, 1961, **8** (2–3), 57–71 (in English).—In the absence of catalyst, quant. recoveries of N were obtained from $(NH_4)_2SO_4$ after digestion for 20 min. with H_2SO_4 containing up to 2·75 g of K_2SO_4 per ml, but losses occurred when the concn. was increased to 3·0 g per ml; quant. recoveries were also obtained from *S*-benzylisothiuronium chloride, but not from nicotinic acid. The most effective catalyst was HgO, which did not cause losses during the digestion of $(NH_4)_2SO_4$ and led to good recoveries from nicotinic acid. The other catalysts that were examined [Se, H_2SeO_3, H_2SeO_4, $CuSO_4$, TiO_2, $FeCl_2$, $FeSO_4$, $Fe_2(SO_4)_3$, H_2PtCl_6, MoO_3, V_2O_5, $VOSO_4$, CrO_3 and Te] gave low recoveries from nicotinic acid, or from $(NH_4)_2SO_4$, or both. Some combinations of catalysts (HgO - Se, HgO - Te) were satisfactory, but did not have any advantages over HgO alone. For a 5-mg sample, a digestion mixture consisting of HgO (20 mg), K_2SO_4 (2·25 g) and H_2SO_4 (1·5 ml) is recommended. This mixture was suitable for the digestion of a wide variety of organic nitrogen compounds.

R. M. ROWLEY

4207. **Determination of nitrogen with gas chromatography.** R. H. Reitsema and N. L. Allphin (Denver Res. Center, The Ohio Oil Co., Littleton, Colo., U.S.A.). *Anal. Chem.*, 1961, **33** (3), 355–359.—Two methods, which combine combustion and gas-chromatographic techniques, are described for application to organic compounds: one gives a ratio of carbon to nitrogen and the other gives an absolute nitrogen determination. The first method, which is based on a comparison of peaks from CO_2 and NO_2, is suitable for use with unweighed samples of pure compounds and of relatively complex mixtures. In the second method, the chromatographic signal due to CO_2 is masked by the use of CO_2 as carrier gas, so that only one peak (NO_2) is observed. This method is suitable for application to samples containing many components and to pure materials. Results from both methods are compared with those from the Kjeldahl method and agreement is very good. Some results are given for nitrogen determinations in shale-oil fractions.

C. B. BAINES

4208. **New method for detecting nitrogen in organic substances.** A. Spěvák, V. Kratochvíl and M. Večeřa (Res. Inst. of Org. Synth., Pardubice-Rybitví, Czechoslovakia). *Coll. Czech. Chem.*

Commun., 1961, **26** (3), 887–890 (in German).—After fusion of the sample with sodium, the CN^- are converted with HCl and chloramine T into CNCl, which gives the characteristic colours of polymethine dyes with dimedone in pyridine. The method gives positive results when Lassaigne's test fails and is sensitive down to 0·02 μg of CN^- per ml. *Procedure*—Fuse the sample (1 to 2 mg) with sodium (0·1 to 0·2 g) in the usual manner, add 5 ml of water, and filter. Dilute to 10 ml. To 1 ml add 1% chloramine-T soln. (1 ml) and N-HCl (1 ml), shake for 1 min., and add 3 ml of a 3% soln. of dimedone in 30% aq. pyridine. The colour produced passes from orange, through violet (stable for 10 min.) to blue (which fades). J. P. STERN

4209. **Quantitative determination of quinone groups. Application to a series of quinones and to a pyridine extract of coal.** S. Delavarenne, A. Halleux and H. Tschamler (European Res. Ass. S.A., Brussels, Belgium). *Rec. Trav. Chim. Pays-Bas*, 1961, **80** (1), 27–42.—The reduction of several quinones and acetylated quinones by Brockmann and Budde's method (*Chem. Ber.*, 1953, **86**, 432) with zinc and acetic anhydride leads to reduction and acetylation of the quinone group. A study of the i.r. spectra of some of the compounds before and after reductive acetylation shows the disappearance of the quinone band at 5·9 μ. Application of this method to the pyridine extract of a vitrinite leads to a lower acetyl number of the product than is expected owing to a hydrogenolysis of acetyl groups by moisture present, and possibly also to scission at heterocyclic N atoms. Reduction by the method of Von (U.S. Patent 2,660,580) by copper powder and H_2S in pyridine soln., followed by acetylation, gives similar results for the model compounds, but leads to no scission in the pyridine extract. It is shown that the contribution of the quinone groups to the i.r. band at 6·2 μ is not as important as has been supposed. E. J. H. BIRCH

4210. **Amperometric argentimetric and mercurimetric titration of sulphydryl. II. Mercurimetric titration.** I. M. Kolthoff and J. Eisenstädter (Sch. of Chem., Univ. of Minnesota, Minneapolis, U.S.A.). *Anal. Chim. Acta*, 1961, **24** (3), 280–293 (in English).—The ampero-mercurimetric titration of cysteine, glutathione, thioglycollic acid and 2-mercaptoethanol has been studied with two electrode systems. At pH 9 with the rotated mercury-pool electrode, sharp end-points corresponding to the composition $(XS)_2Hg$ are obtained, while at pH 2 in the presence of 0·01M-SO_3, accurate determination of thiols such as cysteine is possible; the error is + 1%. P. D. PARR-RICHARD

4211. **Determination of micro amounts of carbon monoxide in ethylene [by gas chromatography].** P. I. Markosov, V. N. Zaĭchenko and Z. A. Lityaeva (Krasnodar Filial of the All-Union Sci. Res. Petroleum Gas Inst.). *Zavod. Lab.*, 1961, **27** (3), 285–287.—The method is based on adsorption of CO (< 0·001%) on activated charcoal and fractional desorption in a current of air.
G. S. SMITH

4212. **Oxidimetric determination of n-butyllithium in hydrocarbons using vanadium pentoxide.** P. F. Collins, C. W. Kamienski, D. L. Esmay and R. B. Ellestad (Res. Lab., Lithium Corp. of America, Inc., Bessemer City, N.C., U.S.A.). *Anal. Chem.*, 1961, **33** (3), 468–470.—A simpler method than the double-titration procedure of Gilman and Haubein (*cf. J. Amer. Chem. Soc.*, 1944, **66**, 1515) is proposed. *Procedure*—Weigh 6 g of V_2O_5 (dried at 150° for several hours) into a dry 250-ml Erlenmeyer flask fitted with a rubber stopper having inlets for Ar and the sample. Add 30 ml of n-heptane, stopper the flask and flush with Ar for 10 min. Add a 5-ml sample of the alkyl-lithium soln. (up to 2·5M), swirl vigorously and allow to stand for 10 min., under an atmosphere of Ar. Add 15 ml of 10% H_2SO_4 and 100 ml of boiling H_2O and titrate while still hot with standard sulphatoceric acid soln. (preparation described), and determine the end-point potentiometrically with a platinum electrode and a normal calomel or silver - silver chloride reference electrode. The method yields reasonably accurate results, even in the presence of large amounts of alkoxide. Only n-, s-, and t-butyl-lithium and ethyl-lithium compounds have been assayed, but the method should be applicable to any alkyl-lithium compound in a hydrocarbon solvent. R. A. HENDEY

4213. **Quantitative analysis by infra-red absorption of trichloroethane [containing di- and tetrachloroethanes].** V. I. Kolbasov, S. B. Bardenshteĭn and R. V. Dzhagatspanyan. *Zavod. Lab.*, 1961, **27** (3), 295–296.—Analysis of four-component mixtures in CCl_4 soln. is carried out from measurements of the absorption bands at 883 cm^{-1} (1,2-dichloroethane), 934 cm^{-1} (1,1,2-trichloroethane), 960 cm^{-1} (1,1,1,2-tetrachloroethane) and 1017 cm^{-1} (1,1,2,2-tetrachloroethane). G. S. SMITH

4214. **Gas - liquid chromatography of fatty derivatives. IV. Quantitative analysis of normal alcohols.** W. E. Link and R. A. Morrissette (Archer-Daniels Midland Co., Minneapolis, Minn., U.S.A.). *J. Amer. Oil Chem. Soc.*, 1960, **37** (12), 668–671.—The C_8 to C_{18} normal alcohols are separated by this technique by the use of acid-washed Chromosorb W (40 to 60 mesh) that has been treated with methanolic KOH soln. After removal of the methanol in a vacuum oven at 80°, the support is impregnated with Apiezon L in a 5:1 ratio. A stainless-steel column (2 ft. × 0·25 in. outside diam.) is packed with this support, and used with He as carrier gas at 180° to 230°. The response of the detector is an approx. linear function of the chain length of the alcohol. A statistical comparison has been made of the accuracy of results obtained with model mixtures. G. R. WHALLEY

4215. **Characterisation of hydroxyl compounds. Identification of their 3,5-dinitrobenzoate esters by X-ray diffraction.** K. J. Garska, R. C. Douthit and V. A. Yarborough (Devel. Dept., Union Carbide Chemicals Co., S. Charleston, W. Va., U.S.A.). *Anal. Chem.*, 1961, **33** (3), 392–395.—Detailed descriptions are given for obtaining and using the X-ray diffraction patterns of the 3,5-dinitrobenzoates of 24 alcohols containing from 1 to 22 carbon atoms. The technique makes possible the identification of hydroxyl compounds that cannot be examined readily by other techniques, such as gas chromatography and mass spectrometry. For qual. and semi-quant. analysis of alcoholic mixtures, this technique may be used, combined with infra-red spectrometric techniques. C. B. BAINES

4216. **Determination of ethanol, 2-ethoxyethanol and water when present together.** L. G. Afanas'eva. *Trudy Khim. i Khim. Tekhnol.*, 1959, (3), 615–618; *Ref. Zhur., Khim.*, 1961, (4), Abstr. No. 4D137.—A refractometric method is proposed for the

analysis of ternary mixtures having an ethanol (**I**) content of 40 to 90% and a 2-ethoxyethanol (**II**) content of 2 to 20%. Prepare artificial mixtures containing an equal amount of **II** and different amounts of **I** and H_2O; measure their refractive indices (n) at 20° and construct curves of n *vs.* the **I** plus **II** content. Determine the H_2O content of the test mixture by the Karl Fischer method; calculate the **I** plus **II** content by difference and determine the n of the mixture. Construct a curve relating n to the **II** content of the mixture with a given **I** plus **II** content, and find the **II** content from it; determine **I** by difference. The method was tested with 5 artificial mixtures; the absolute error was $\not> \pm 2\%$. Five industrial mixtures were determined by the refractometric method and by the distillation method; lower results were obtained with the latter. The method can be used to control the manufacture of **II**; acetaldehyde does not interfere. K. R. Cook

4217. **Primary amyl alcohols determined by gas chromatography.** P. J. Porcaro and V. D. Johnston (Anal. Lab., The Givaudan Corp., Delawanna, N.J., U.S.A.). *Anal. Chem.*, 1961, **33** (3), 361–362.—Mixtures of primary amyl alcohols were separated by using a column of copper tubing (10 to 21 ft. × 0·25 in.) packed with the synthetic detergent Tide (40 to 60 mesh, and dried overnight at 110°). The carrier gas was He, at a rate of 15 ml per min. inlet, and 30 ml per min. outlet. The column temp. was 160°. Known mixtures were analysed, and the percentage composition was calculated with the rectangular method of geometric approximation. Mixtures of the pure primary alcohols gave reproducible results within $\pm$ 0·5% for each component. Good separation was attained for 2-methylbutan-1-ol and 3-methylbutan-1-ol, previously not easily separated. The procedure is applicable to materials of importance in the perfume and flavour industry, *e.g.*, methylionone isomers and terpene alcohols. R. A. Hendey

4218. **Colorimetric determination of 1-chloro-2-propanol with ceric ammonium nitrate.** V. Kapišinská (Res. Inst. Petrochem., Nováky, Czechoslovakia). *Chem. Zvesti*, 1961, **15** (3), 231–234.—*Procedure*—To the sample (10 ml) (containing 2 to 4% of 1-chloro-2-propanol) add 0·36N-$(NH_4)_2Ce(NO_3)_6$ (4 ml), mix, and measure the extinction of the orange soln. at 500 mμ with a blue filter. Compare with a calibration curve. The method is suitable for soln. of samples of pH 7. The mean error is $\pm$ 1%. J. Zýka

4219. **The qualitative and quantitative determination of sugars by means of silica-gel film chromatography. II.** G. Pastuska (Bundesanstalt f. Materialprüfung, Berlin-Dahlem, Germany). *Z. anal. Chem.*, 1961, **179** (6), 427–429 (in German).—The sugars are separated on borate-buffered silica-gel films and determined by oxidation with $K_2Cr_2O_7$. *Procedure*—On each glass plate (6 cm × 12 cm) spread a mixture of Kieselgel G (Merck) (4 g) and 0·1N-H_3BO_3 (6 ml). Dry in air for 45 min. and then at 105° for 30 min. This gives a film thickness of $\simeq$ 0·9 mm. Mark the origin and suspend the plates vertically in the (ascending) solvent (20 ml for 2 plates). The solvents used are benzene - acetic acid - methanol (1:1:3) and ethyl methyl ketone - acetic acid - methanol (3:1:1). For qual. purposes, use $\simeq$ 40 μg of sugar and chromatograph for $\simeq$45 min. (the solvent front moves 10 cm). Dry in warm air and detect with aniline phthalate or spray with 20% H_2SO_4 - 0·2% ethanolic 1,3-dihydroxynaphthalene (1:1) and dry at 105°. The latter reagent also detects disaccharides and uronic acids. R_F values are given for 12 compounds in the 2 solvents. For quant. purposes, cut out the desired area of film together with a similar sugar-free area at the same distance from the origin for use as a blank. Heat the silica gel with a twofold excess of acid $K_2Cr_2O_7$ soln. [0·05 or 0·01N in 70% (w/w) H_2SO_4] for 60 min. on a water bath. Cool, dilute with H_2O (20 ml), add 5% KI soln. (5 ml), set aside for 2 min. and then titrate with 0·01N-$Na_2S_2O_3$. Since the reaction is only 97 to 98% complete, the $K_2Cr_2O_7$ soln. is standardised against glucose. G. Russell

4220. **Complexometry in organic analysis. IX. Determination of aldehydes, hydroxylamine, hydrazine and their derivatives by oxidation with the mercury(II) salt of EDTA.** B. Buděšínský (Res. Inst. f. Pharmacy and Biochem., Prague). *Coll. Czech. Chem. Commun.*, 1961, **26** (3), 781–787 (in German).—The organic reducing agents are oxidised with Hg^{II} - EDTA in 0·2M to 2M-KOH and the liberated EDTA is determined by titration with 0·05M-$Pb(NO_3)_2$, with methylthymol blue as indicator. The method, on 10 mg of organic material, is accurate to within $\pm$ 1%. Side-reactions interfere in the determination of acetaldehyde. J. P. Stern

4221. **Chromatography of organic substances. VIII. Separation of aldehydes and ketones after condensation with cyanoacetohydrazide.** J. Franc and G. Čelikovská (Res. Inst. of Org. Syntheses, Pardubice-Rybitví, Czechoslovakia). *Coll. Czech. Chem. Commun.*, 1961, **26** (3), 667–672 (in German).—A useful spread of R_F values (tabulated for 50 compounds) is shown by the cyanoacetic acid hydrazones of carbonyl compounds. These are submitted to descending chromatography on paper impregnated with formamide, dimethylformamide or acetamide, with chlorobenzene as mobile phase. A separation at 20° takes 2 hr. J. P. Stern

4222. **Polarographic determination of dichloroacetaldehyde in the products of chlorination of ethanol.** N. P. Romazanovich and K. G. Berezina. *Zavod. Lab.*, 1961, **27** (3), 287–290.—By fractional distillation and measurements of the differential wave peaks at $E_{\frac{1}{2}} = -1{\cdot}1$ and $-1{\cdot}62$ V in KCl soln., together with the use of calibration curves for various contents of dichloroacetaldehyde (**I**) and chloral hydrate, the content of **I** can be determined. G. S. Smith

4223. **Fluorimetric detection and determination of organic compounds. I. A rapid micro semi-quantitative test for acetone and some spectrophotofluorimetric data on this detection.** R. Brandt and N. D. Cheronis (Dept. Chem., Brooklyn College, New York). *Microchem. J.*, 1961, **5** (1), 110–114.—The rapid formation of an azine, which exhibits a bright-yellow fluorescence when exposed to u.v. light, by the combination in $CHCl_3$ soln. of 2-diphenylacetylindane-1,3-dione 1-hydrazone (*cf.* Braun and Mosher, *J. Amer. Chem. Soc.*, 1958, **80**, 3048) with acetone, has been utilised for the detection and semi-quantitative determination of acetone. A visually detectable u.v. fluorescence was given by the azine derived from acetone (0·058 μg) in $CHCl_3$ (1·5 ml), and preliminary experiments with a spectrofluorimeter have shown

that rapid quantitative reactions take place with concn. of acetone down to 10^{-4}M, and the lower limit of detection of the azine is 10^{-5} μg per ml. The azine has a fluorescence peak at 525 mμ and activation peaks at 295 and 415 mμ.
I. A. SIMPSON

4224. **Butyltriethylammonium hydroxide as titrating agent for the potentiometric determination of weak acids in non-aqueous solvents.** P. Fijolka and I. Lenz (Inst. f. Kunstoffe, Dtsch. Akad. Wissenschaft., Berlin). *Plaste u. Kautsch.*, 1960, **7** (4), 169–170.—Comparison has been made of butyltriethylammonium hydroxide and Na ethoxide for the titration of adipic acid and polyesters in org. solvents. The advantage of the former titrant is the high solubility of its salts in org. solvents, but disadvantages are the formation of H_2O in the titration and, particularly, the poor stability of 0·01N soln.
L. A. O'NEILL

4225. **Effect of structure on the stereochemistry of electrode reactions. Monobromo C_4 dibasic acids and esters.** P. J. Elving, I. Rosenthal, J. R. Hayes and A. J. Martin (Univ. of Michigan, Ann Arbor, U.S.A.). *Anal. Chem.*, 1961, **33** (3), 330–334.—Bromomaleic acid (**I**) and bromofumaric acid, their diethyl esters and bromosuccinic acid have been polarographically and coulometrically reduced between pH 0·5 and 10·5. The reduction products were identified polarographically, and, on a macro scale, by chemical and physical methods. In the reduction of **I**, a dimer is formed which is the first reported case of dimer production in an aliphatic compound by electrochemical carbon - halogen bond fission. This is postulated as proof of a free-radical intermediate. Reduction mechanisms are proposed to explain the products observed in all the reactions.
R. A. HENDEY

4226. **Determination of 2-nitropropane and of nitrite in mixtures.** F. L. Estes and P. K. Baughman (Biochem. Dept., Baylor Univ. Coll. of Med., Houston 25, Texas, U.S.A.). *Anal. Chem.*, 1961, **33** (3), 473–475.—It is necessary to separate 2-nitropropane (**I**) from nitrites (**II**) in mixtures because of cross-interference in the final determination of each. *Procedure*—Extract 1·5 ml of the aq. soln. of **I** and **II** with 1 to 5 ml of heptane or benzene. Determine **II** on an aliquot (0·4 to 0·7mM in **II**) of the aq. layer by the sulphanilamide method. To an aliquot of the organic layer (containing 0·2 to 22 μmoles of **I**) add 5 ml of H_2O and 1·0 ml of 6·3M-NaOH. Shake well, set aside for 10 min., then add 0·5 ml of 30% H_2O_2 soln. Heat the mixture in a loosely stoppered tube for 1 to 1·5 hr. in a water bath. Cool, dilute to 10 ml and determine **II** as already described. The recovery of aliphatic nitro-compounds is limited by the solvent. Benzene removes both 1-nitropropane and **I**, but is not suitable for nitroethane or nitromethane. Heptane is effective for up to 10 μmoles of nitroethane, but not for 1-nitropropane or nitromethane.
R. A. HENDEY

4227. **Detection and determination of ammonium compounds in urea.** H. Moll (Inst. f. Verfahrenstechnik d. org. Chem., Leipzig, Germany). *J. prakt. Chem.*, 1961, **12** (3–4), 121–133.—Ammonium compounds are detected by pptn. with Na tetraphenylborate, which is not affected by urea. The ppt. is identified by filtering, treating it on the filter-paper with alkali in a Petri dish and detecting NH_3 with litmus paper and Nessler reagent; a blank must be performed on pure urea. Ammonium salts of strong acids in urea are determined directly by conductimetric titration; for salts of weak acids, *e.g.*, carbonic and carbamic, mineral acid is added before the titration. Mention is made of a modified Conway diffusion method and also of an ion-exchange method in which NH_4^+ are removed on the column and the urea is determined bromatometrically or enzymatically; the biuret content must not exceed 1%.
J. H. WATON

4228. **Polarographic resolution of mixtures of complexans.** W. Hoyle, I. P. Sanderson and T. S. West (Univ., Birmingham, England). *J. Electroanal. Chem.*, 1961, **2** (2), 166–173 (in English).—By the addition of just sufficient Cu^{2+} to react with all the complexans, and subsequent examination by derivative polarography, it is possible to resolve binary mixtures of the more common complexans and, in certain favourable cases, ternary mixtures. In order to obtain satisfactory resolution, the $E_{\frac{1}{4}}$ of the Cu chelates *vs.* the S.C.E. must differ by at least 50 mV, corresponding to a difference of 2 to 3 units in the values of log K; semi-quant. analysis is also possible when reasonable resolution is achieved.
T. R. ANDREW

4229. **Gas-chromatographic separation of organic sulphides.** J. Petránek (Res. Inst. Org. Synth., Pardubice-Rybitví, Czechoslovakia). *J. Chromatography*, 1961, **5** (3), 254–258 (in German).—The gas-chromatographic separation and identification of C_1 to C_4 dialkyl sulphides and C_1 to C_4 alkyl benzyl sulphides, with silicone oil and 5,6- and 7,8-benzoquinolines as stationary phases, is described. Selective separation of branched-chain from normal alkyl sulphides is achieved with the benzoquinolines, whilst with silicone oil, separation is according to boiling-points. Experimental results and conditions are given for these separations.
G. P. MITCHELL

4230. **Iodimetric determination of "dixanthogen".** V. R. Satyanarayana Rao and A. R. Vasudeva Murthy (Dept. of Inorg. and Phys. Chem., Indian Inst. of Science, Bangalore, S. India). *Chemist Analyst*, 1961, **50** (1), 32.—When treated with SO_3^{2-}, each mole of *OO*-diethyl dithiobisthioformate [dixanthogen] is decomposed into 2 moles of $S_2O_3^{2-}$, which are titrated iodimetrically. *Procedure*—The sample (0·5 g) is dissolved in 100 ml of ethanol or methanol and a 5-ml aliquot is taken; M-Na_2SO_3 (5 ml) is added and the mixture is shaken for 5 min., made homogeneous by adding water and set aside for 30 min. The excess of SO_3^{2-} is fixed with 10 ml of 40% formaldehyde soln. and 3 ml of glacial acetic acid. The soln. is diluted to 200 to 300 ml with water and titrated with iodine and starch.
J. H. WATON

4231. **Paper chromatography of some sulphinic acids and sulphonyl chlorides.** L. Gringras and G. Sjöstedt (AB Caeverken, Strängnäs, Sweden). *Acta Chem. Scand.*, 1961, **15** (2), 435–436.—Alkyl- and aryl-sulphinic acids and sulphonyl chlorides can be separated and quantitatively determined by chromatography on paper by an ascending technique with n-butanol - n-propanol - water (1:1:1) as solvent. The starting point for samples containing sulphonyl chlorides is marked, and pre-treated with an alkaline Na_2SO_3 soln. before application of the sulphonyl chlorides, which are immediately converted into the sulphinic acid salts. The spots are revealed by spraying with a 0·25 to

0·5% soln. of zinc chloride-stabilised tetrazotised *o*-dianisidine (Fast blue salt B) (C.I. Azoic Diazo Component 48), which gives yellow spots insol. in water but sol. in benzene. This reaction is specific for the sulphinic acid group. As little as 4 μg of sulphinic acid and 100 μg of sulphonyl chloride can be detected. S. M. MARSH

4232. **Colorimetric determination of trichlorosilane in air.** F. D. Krivoruchko (Inst. of Work Hygiene and Occupational Diseases). *Zavod. Lab.*, 1961, **27** (3), 290–291.—The method is based on the formation and simultaneous reduction to molybdenum blue of the heteropoly-acid formed by reaction of trichlorosilane with a 5% soln. of $(NH_4)_2MoO_4$ in acetic acid. An editorial note suggests that the method is not specific for trichlorosilane. G. S. SMITH

4233. **Potentiometric determination of chlorine bound to boron in mixtures containing 2-chlorovinyl boron chlorides and ethyl boron chlorides.** H. G. Nadeau, D. M. Oaks and R. D. Buxton (Olin Mathieson Chemical Corp., New Haven, Conn., U.S.A.). *Anal. Chem.*, 1961, **33** (3), 341–342.—An accurate method is described for the determination of Cl bound to boron in organoboron compounds containing both boron - chlorine and carbon - chlorine bonding. The compounds, or mixture of compounds, are dissolved in HNO_3 - methanol (1:2) in the absence of air. The mixture is set aside for 10 min., and the HCl formed through esterification of the Cl bound to boron is titrated potentiometrically with standard $AgNO_3$ soln. The Cl bound to boron in the chloro-2-chlorovinylborines and in the chloroethylborines esterifies quantitatively, and the 2-chlorovinyldimethoxyborine formed is stable in this medium. The method gives reproducible results and shows good accuracy over a wide range of concentration. R. A. HENDEY

4234. **Spectrophotometric determination of dibutyltin dichloride.** R. T. Skeel and C. E. Bricker (Dept. of Chem., Princeton Univ., N.J., U.S.A.). *Anal. Chem.*, 1961, **33** (3), 428–431.—The method described, which is based on the reaction of dibutyltin dichloride (**I**) with diphenylcarbazone (**II**) to give a coloured complex with an absorption max. at 530 mμ, is applicable to the determination of small amounts of **I** in the presence of more than a 100-fold excess of mono-, tri- and tetra-butyltin compounds. *Procedure*—Add 1 to 6 ml of the organotin compounds (containing 3 to 150 μg of **I**) in $CHCl_3$ to 10 ml of EDTA soln. [4 g of disodium salt per litre, buffered (1:1) with trichloroacetic acid - NaOH (pH 1·80 ± 0·05); the pH is then adjusted to 2·05 ± 0·02]. Adjust the vol., if necessary, to 6 ml with $CHCl_3$. Shake the mixture gently 30 times, and then draw off the $CHCl_3$ into 10 ml of fresh EDTA soln. and shake again. Repeat again with fresh EDTA soln., then add the $CHCl_3$ layer to 5 ml of 0·2N-trichloroacetic acid adjusted to pH 1·80 ± 0·05. Add 5 ml of **II** soln. (0·2% in $CHCl_3$) and shake gently ≃ 50 times. Add sufficient of this $CHCl_3$ layer to 5 ml of ethanol to make the vol. 10 ml, and measure the extinction of the soln. at 400 mμ (for **II** alone) and at 530 mμ (for the complex and **II**). The extinction of **II** has to be subtracted from the results. Beer's law is obeyed over the range 2·7 to 137 μg of **I**. When butyltin trichloride and potentially interfering inorganic ions (Zn^{2+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Pb^{2+}, Cu^{+}, Cu^{2+}, Cd^{2+}, Sn^{2+} and Sn^{4+}) are absent, the EDTA extraction may be omitted. R. A. HENDEY

4235. **Paper-chromatographic detection of some symmetrical and asymmetrical alkyl-lead compounds.** H. Schäfer (Inst. f. Med. u. Biol., Dtsch. Akad. Wiss., Berlin). *Z. anal. Chem.*, 1961, **180** (1), 15–18 (in German).—Trialkyl-lead chlorides and bromides are separated. Two solvents are used—(*i*) benzene (6 vol.) and cyclohexane (3 vol.) are mixed and saturated with water; the organic phase is filtered through a paper wetted with benzene and mixed with acetic acid (1 vol.); (*ii*) cyclohexane is saturated with water. The bottom of the tank is covered with water. Ascending development on S. & S. 2043b paper is used and 5 μl of soln. (containing ≃ 20 μg of Pb) is applied. The solvent front is allowed to travel 23 to 25 cm. After a 10-min. irradiation with u.v. light, the compounds are detected by spraying with $(NH_4)_2S$ soln. R_F values for several compounds in the two solvents are tabulated. The water content of the solvents is critical: a lower water content leads to an increase in R_F, especially for slowly moving components. Better separation is obtained with chlorides than with bromides. G. RUSSELL

4236. **Determination of methyl groups in alkylbenzenes by chromic acid oxidation.** S. G. Brandenberger, L. W. Maas and I. Dvoretzky (Shell Oil Co., Houston Res. Lab., P.O. Box 100, Deer Park, Tex., U.S.A.). *Anal. Chem.*, 1961, **33** (3), 453–455.—A modification of the Kuhn - Roth method for the determination of C-methyl groups in alkylbenzenes is given. The sample (20 to 30 mg) is weighed into a tube, and 6·67 ml of 5N-chromic acid and 3·33 ml of H_2SO_4 are added. The tube is sealed and the contents are digested for 3 hr. at 130° ± 1°, with constant shaking. The resulting mixture is steam-distilled and the products are analysed. Under these conditions benzoic acid is destroyed and yields of acetic acid are good for side-chain oxidation of pure alkylbenzenes. For poly-substituted and fused-ring mono-aromatic systems, the yield of acetic acid was about 70 to 85%, based on the total number of methyl groups present. Studies with polyalkylbenzenes and mono-aromatic petroleum fractions show that there is a systematic increase in methyl groups with increase in mol. wt. R. A. HENDEY

4237. **Gas - liquid chromatographic analysis of trace impurities in styrene by using capillary columns.** O. L. Hollis (Organic Basic Res. Lab., Texas Div., The Dow Chemical Co., Freeport, U.S.A.). *Anal. Chem.*, 1961, **33** (3), 352–355.—Use is made of capillary columns in conjunction with a triode argon detector to separate and detect xylenes and other impurities (in concn. < 25 p.p.m.) in finished styrene without a concentration step. The method is rapid and sensitive. Relative retention times of 25 known and suspected impurities are given for three columns of stainless steel with bis(phenoxyphenyl) ether, Ucon 50-HB-2000 and Apiezon L as liquid phases. All the columns can be used up to 200°, with a sample of 0·005 μl. C. B. BAINES

4238. **Quantitative analysis of phenols by gas chromatography.** H. Weiss and A. Kreyenbuhl (Cerchar, Lab. de Verneuil-en-Halatte, Oise, France). *Bull. Soc. Chim. France*, 1961, (3), 603–606.—In the gas-chromatographic analysis of a

mixture of phenols (*cf.* Kreyenbuhl and Weiss, *Anal. Abstr.*, 1960, **7**, 5297) it has been found that the specific peak area decreases with retention time. The extent of this phenomenon has been studied and it is recommended that for a complicated mixture of phenols a rough analysis should first be made with an internal standard, and the mixture then analysed with a separate internal standard for each component. Each standard should be similar in chemical type and concn. to the corresponding component, and should form a peak close to that component. G. BURGER

4239. **Gas-chromatographic analysis of phenol - cresol - xylenol mixtures with special reference to the o-cresol content of tritolyl phosphate.** K. Wrabetz and W. Sassenberg (Org. Anal. Lab., Farbenfabriken Bayer A.-G., Leverkusen, Germany). *Z. anal. Chem.*, 1961, **179** (5), 333–342 (in German). —Simplified conditions have been adopted. *Procedure*—A column of acid-washed Chromosorb R (Johns Manville) (0·3 to 0·4 mm), treated with dinonyl phthalate, is packed in a U-tube, 300 cm × 0·48 cm, to a density of 46 g per 100 ml. The carrier gas is H at 230 ml per min., the working temp. is 144° (*o*-xylene vapour), and detection is by thermal conductivity. It is advantageous to mix the sample with 0·5 vol. of acetone as a marker; 5 to 10 μl of this soln. is used. Good separation of 12 phenols is achieved, except for the pairs 2,4- and 2,5-xylenol and *m*- and *p*-cresol. Better separation of the latter pair is achieved with di-[*cis*(I + II)-decahydro-2-naphthyl] phthalate as stationary phase. A table of quant. results calculated from peak areas is given; the error rarely exceeds 4%. For the *o*-cresol determination, the phenols are isolated from the ester in dichloromethane soln. (Stoltenberg, *Ibid.*, 1955, **146**, 181) and the above procedure is then applied. Apart from the cresols, at least 4 other phenols may be present. The detection limit for *o*-cresol is ≃ 0·05%.
G. RUSSELL

4240. **Simple gas-chromatographic determination of the o-cresol component of tritolyl phosphate.** H. Rohleder (Farbwerke Hoechst A.-G., Frankfurt-am-Main-Höchst, Germany). *Z. anal. Chem.*, 1961, **180** (1), 32–35 (in German).—A scheme has been worked out for the determination of the toxic *o*-cresol in technical tritolyl phosphate in the presence of phenol, ethylphenols and xylenols. *Procedure*—Saponify the ester (3 g) with alkaline ethanediol (25 g of KOH plus 25 ml of ethanediol) (50 g) for 15 min., slowly add water (400 ml) and acidify with 20% H_2SO_4 (120 ml). Cool and extract thrice with dichloromethane (100, 50 and 50 ml). Transfer the extracts to a distillation flask (500 ml) and fractionate through a short column at a reflux ratio of 1:3 till ≃ 50 ml remains. Dry this with anhyd. Na_2SO_4 (5 g) and repeat the distillation till ≃ 3 ml remains. Add *p*-dichlorobenzene as a marker. The column conditions are as follows—column, 10 metres × 4 mm copper tubing; packing, siliconised Chromosorb with 20% DC 550 silicone oil; column temp., 185°; carrier gas, H at 2·4 atmospheres; sample volume, 10 μl. The apparatus used was the Perkin - Elmer model 116 with thermal-conductivity detection. The *p*-dichlorobenzene was eluted at 30 min., and the concn. was calculated from the peak area. A coeff. of variation of ≃ ± 4% was obtained. *m*-Cresol and *p*-cresol may be determined by i.r. absorption after dissolution in CS_2.
G. RUSSELL

4241. **Effect of substitution on the fluorescence of phenol and aniline.** A. Rosen and R. T. Williams (Dept. Biochem., St. Mary's Hosp. Med. Sch., London, England). *Photoelect. Spectr. Gr. Bull.*, 1961, (13), 339–345.—Measurements are reported on the fluorescence of methyl- and carboxyl-substituted phenols and of methyl-, carboxyl- and chloro-substituted anilines in aqueous solution at different pH values. G. SKIRROW

4242. **Silica-gel-film chromatography of phenols and phenolcarboxylic acids. I.** G. Pastuska (Bundesanst. f. Materialprüfung, Berlin-Dahlem, Germany). *Z. anal. Chem.*, 1961, **179** (5), 355–358 (in German).—Chromatography is carried out on thin films (≃ 0·5 mm) of Kieselgel G (Merck) supported on glass plates. *Procedure*—Mark the origin with a needle, load with the test substances (≃ 10 μg of each) and suspend the plate vertically in the solvent. Develop with benzene - dioxan - acetic acid (90:25:4) or benzene - methanol - acetic acid (45:8:4) by the ascending technique. A time of 40 min. (≃ 10 cm travel) is usually sufficient. Dry the chromatogram with warm air and reveal the spots. A table is given of R_F values for the 2 solvents, and colours produced by 5 different reagents [tetrazotised benzidine, diazotised sulphanilic acid, Fast red salt B (C.I. Azoic Diazo Component 5), Fast blue salt B (C.I. Azoic Diazo Component 48) and Fast blue salt BB (C.I. Azoic Diazo Component 20)] with 22 compounds. R_F values are claimed to be reproducible to within ± 0·02 and the detection limit is ≃ 4 μg. The silica-gel films are claimed to give better resolution than paper, and to allow greater freedom in the choice of reagent.
G. RUSSELL

4243. **Spot tests for dihydroxybenzenes.** T. S. Ma and A. Hirsch (Brooklyn Coll., Brooklyn, New York). *Chemist Analyst*, 1961, **50** (1), 12–13.—*Procedure*—The sample is dissolved in the minimum amount of acetone - H_2O (1:1) and the pH is adjusted to 5 with 6M-acetic acid. A few drops of soln. are placed on each of 2 pieces of filter-paper and air-dried, and 3 drops are placed on a spot-plate. The first piece of paper is tested with a drop of Hg^I soln. [28 mg of $Hg_2(NO_3)_2.2H_2O$ per ml]. A rust-brown colour indicates resorcinol. The second piece is tested with a drop of cyanide soln. (38 mg of NaCN per ml). A green spot with dark-brown edges indicates quinol. The drops on the plate are tested with dichromate soln. (20 mg of $K_2Cr_2O_7$ per ml). A light-orange colour changing quickly to dark-brown or black indicates catechol. The presence of 25 μg of one isomer can be detected in the presence of a 400-fold excess of the others. The dilution limit is ≃ 500 p.p.m. Diamino-, triamino- and trihydroxy-benzenes do not interfere; the effect of other phenolic compounds has not been investigated. J. H. WATON

4244. **Correlation of mass spectra with structure in aromatic oxygenated compounds. Methyl-substituted aromatic acids and aldehydes.** T. Aczel and H. E. Lumpkin (Res. and Devel. Div., Humble Oil & Refining Co., Baytown, Tex., U.S.A.). *Anal. Chem.*, 1961, **33** (3), 386–389.—Correlations between mass-spectra data and chemical structure are studied in detail for several aromatic mono-, di- and poly-carboxylic acids and aldehydes. Emphasis is given to the study of ions that can be used for qual. and quant. analysis, and peak-heights are given as a percentage of total ionisation for a large number of acids and aldehydes. The

study confirms that the respective positions of the various substituents on the benzene ring play a leading part in the formation of fragment ions.
R. A. HENDEY

4245. **Potentiometric determination of arylsulphinic acids.** L. Gringras and G. Sjöstedt (AB Caeverken, Strängnäs, Sweden). *Acta Chem. Scand.*, 1961, **15** (2), 433–434.—The use of $Ce(SO_4)_2$ soln. as titrant in the determination of arylsulphinic acids has been investigated. The sodium and ammonium salts of toluene-*p*-sulphinic acid were used as test substances and the acidified sample soln. was titrated with 0·1N-$Ce(SO_4)_2$ in 1·5N-H_2SO_4. The end-point was detected potentiometrically with a combined platinum - calomel electrode; a sudden jump of 200 mV was observed at the end-point on the addition of a single drop of titrant. Gravimetric experiments have confirmed the stoicheiometry of the reaction and an equation is presented for the calculation of results. S. M. MARSH

4246. **Application of chrono-amperometry by anodic dissolution to the determination of triphenyltin acetate.** P. Nangniot and P. H. Martens (Inst. Sup. Agronom. de l'État, Gembloux, Belgium). *Anal. Chim. Acta*, 1961, **24** (3), 276–279 (in French).—In the determination of Sn in triphenyltin acetate and other fungicides, the limiting concn. is 1·25 μg per ml. This is improved by the use of a hanging-drop electrode at which the ions are reduced in a pre-electrolysis step at −0·7 V *vs.* the silver - AgCl - satd. KCl electrode for 5 min.; the potential is then increased gradually to −0·1 V, and the anodic diffusion current is registered at ≃ −0·45 V. The sample for analysis is obtained by extraction of plant material with $CHCl_3$; the extract is washed with 0·1N-KOH and 0·5N-K tartrate, then mineralised with H_2SO_4 - HNO_3, and the residue is dissolved in 5N-HCl. A peak-height of ≃ 0·3 μA was obtained for a concn. of 0·8 μg of Sn per ml. P. D. PARR-RICHARD

4247. **Tetracyanoethylene chemistry. Indirect photometric determination of anthracene in naphthalene.** G. H. Schenk and M. Ozolins (Dept. of Chem., Wayne State Univ., Detroit 2, Mich., U.S.A.). *Talanta*, 1961, **8** (2–3), 109–115.—Tetracyanoethylene and anthracene form a colourless adduct at room temperature. This compound is also formed when anthracene is added to the red complex formed by tetracyanoethylene and naphthalene. The difference between the extinction of a $CHCl_3$ soln. containing the red complex and the extinction of a similar soln. to which anthracene has been added varies linearly with the amount of anthracene. The method can be used for the determination of 0·01% of anthracene in naphthalene. Benzene and toluene do not interfere; indene, phenanthrene, chrysene and fluoranthene interfere slightly when present in excess. Conjugated dienes such as cyclopentadiene react with tetracyanoethylene, but these can be removed by treatment with maleic anhydride, with which anthracene reacts very slowly. R. M. ROWLEY

4248. **Catalytic alkylation of tetrahydronaphthalenes. IV. Determination of the structure of alkyltetrahydronaphthalenes by infra-red spectroscopy.** N. I. Shuĭkin, V. A. Shlyapochnikov, N. A. Pozdnyak and B. L. Lebedev (N. D. Zelinskovo Inst. Org. Chem., Acad. Sci., U.S.S.R.). *Izv. Akad. Nauk SSSR*, 1961, (3), 466–468.—The infra-red spectra of soln. of some alkyltetrahydronaphthalenes in CCl_4 were examined. A linear relationship was found between the number of methylene groups present and the intensities of the absorption bands at 2930 cm^{-1}, and between the number of methyl groups and the intensities at 2960 cm^{-1}.
J. W. PRICE

4249. **Determination of 1,1′-dianthrimide.** A. A. Cherkasskiĭ and N. P. Vinogradova (K. E. Voroshilov Sci. Res. Inst. of Org. Intermediates and Dyestuffs). *Zavod. Lab.*, 1961, **27** (3), 279–282.—*Photometric method*—The sample (0·1 g) is dissolved in 100 ml of 87% H_2SO_4 and shaken for 5 min. with 20 ml of a soln. of 10·5 g of boric acid in 87% H_2SO_4. After 30 min. at 50° the soln. is cooled and diluted to 250 ml with 87% H_2SO_4. Aliquots (4, 5 and 6 ml) are diluted to 50 ml with 87% H_2SO_4 and the extinctions are measured with a red filter after 1 hr. The results are referred to a calibration curve. *Gravimetric method*—The sample (0·2 g) is dissolved in 40 ml of a chlorobenzene fraction (boiling-range 165° to 175°) at 150°. The cooled soln. is shaken for 10 min. with 40 ml of acetone. The ppt. is collected and washed with 110 ml of acetone, dried under an infra-red lamp and weighed. G. S. SMITH

4250. **Gas - liquid chromatography of terpenes. II. The dehydration products of α-terpineol.** E. von Rudloff (Nat. Res. Counc. Canada, Saskatoon, Sask.). *Canad. J. Chem.*, 1961, **39** (1), 1–12.—The mixture of terpenes in the steam-volatile products from the dehydration of α-terpineol with aq. oxalic acid can be almost completely resolved by gas - liquid chromatography at 90° on a 13-ft. column of Chromosorb W (60 to 80 mesh) impregnated with one-sixth of its wt. of rapeseed oil as liquid phase and with He as carrier. If required, the columns of (*i*) polyester plus polyoxyethylene glycol or (*ii*) polyphenyl ether, as described in Part I (*Anal. Abstr.*, 1961, **8**, 187) can be used to supplement the results. By this means, nine main components [terpinolene, dipentene, α- and γ-terpinene, cineole and *p*-mentha-2,4(8)-dienes] can be quant. determined to within ± 3%, and seven minor components (each in concn. < 0·5%) can be determined semi-quant. in the camphene to *p*-menthene range and in the range between the *p*-menthadienes and unchanged α-terpineol. The retention times on the three columns and the yields obtained are listed, and the isolation and identification of the separate components are described. Because of the presence of small amounts of several isomers, the *p*-menthadienes obtained by these procedures must be fractionated (0·01 to 0·1-g samples) by preparative gas - liquid chromatography. W. J. BAKER

4251. **Volumetric determination of 3-hydroxy-2-methylpyran-4-one (maltol) and related compounds.** H. E. Jungnickel (Lebensmittelchem. u. Chem. Abt. d. Bezirks Hygiene Inst., Frankfurt/Oder). *Pharm. Zentralh.*, 1961, **100** (3), 114–116.—Mix the aq. soln. (20 to 120 ml, containing 1 to 100 mg of maltol) with 25% H_2SO_4 (15 ml) and titrate with 0·01N-$Ce(SO_4)_2$, with ferroin as indicator; recoveries in 15 determinations ranged from 98·5 to 103·5%. Alternatively, mix the sample soln. with 2% $FeCl_3$ soln. (0·1 ml) and N-H_2SO_4 (2 ml), dilute with H_2O to 100 ml, set aside for 7 min. and titrate with 0·01N-$Ce(SO_4)_2$; recoveries in 14 determinations ranged from 97·7 to 102·0%.
A. R. ROGERS

4252. **Spot-test detection of piperidine in the presence of piperazine.** F. Feigl (Lab. da Prod. Mineral, Min. da Agric., Rio de Janeiro, Brazil). *Chemist Analyst*, 1961, **50** (1), 15 and 18.—The acid soln. of the amines is made alkaline with an excess of Na_2CO_3 and is heated to 90° to 100°, when only piperidine is volatilised; sodium 1,2-naphthaquinone-4-sulphonate (**I**) is used for detection. *Procedure*—A drop of sample soln. is treated with 1 to 3 drops of Na_2CO_3 soln. in a micro test-tube, and the soln. is heated in a water bath at 90° to 100°. A piece of filter-paper moistened with a 2·5% aq. soln. of **I** is placed over the mouth of the tube. A red stain appearing on the yellow test-paper in 1 to 2 min. indicates piperidine. By this method 20 μg of piperidine can be detected in the presence of 8000 μg of piperazine.

J. H. WATON

4253. **Spot-test detection of piperazine in the presence of piperidine.** F. Feigl (Lab. da Prod. Mineral, Min. da Agric., Rio de Janeiro, Brazil). *Chemist Analyst*, 1961, **50** (1), 18.—After the piperidine has been volatilised in the presence of excess of Na_2CO_3 at 90° to 100°, the piperazine carbonate in the residue is decomposed at a higher temp. and the piperazine is detected with sodium 1,2-naphthaquinone-4-sulphonate (**I**). *Procedure*—A drop of acid sample soln. is treated in a micro test-tube with one drop of 5% Na_2CO_3 soln., and the tube is placed in a glycerol bath pre-heated to 150°. A test-paper moistened with a 2·5% aq. soln. of **I** is placed over the mouth of the tube, and the temp. of the bath is raised to 200° to 230°. A red-violet to pink stain appearing in 1 to 2 min. indicates piperazine. By this method, 20 μg of piperazine can be detected in the presence of 10,000 μg of piperidine. Ammonium salts and salts of volatile primary arylamines do not interfere.

J. H. WATON

4254. **Quantitative analysis for carbonyl sulphide in natural gas by gas-liquid chromatography.** J. A. Schols (Res. and Devel. Lab., Dow Chemical of Canada, Ltd., Sarnia, Ontario). *Anal. Chem.*, 1961, **33** (3), 359–360.—Carbonyl sulphide (**I**) was separated from natural-gas hydrocarbons on a column packed with 38 g of Kromat FB coated with 30% (w/w) of *NN*-dibutylacetamide. The column was operated at 28°, with He as the carrier gas used at an exit flow-rate of 50 ml per min. The relative retention ratios for **I** and various hydrocarbons are given, and only propene has a value similar to that for **I**. When the propene present is < 0·5%, interference is negligible, and **I** can be detected in the range 25 to 1000 p.p.m. The results are compared with those of mass spectrometry and are in fairly good agreement.

R. A. HENDEY

4255. **Two new instruments for measuring the air content of oil.** A. T. J. Hayward (Fluids Mechanics Div., Nat. Engng Lab., East Kilbride, Glasgow, Scotland). *J. Inst. Petrol.*, 1961, **47** (447), 99–106.—Two simple robust instruments are described. Both depend on the admission of a sealed sample of oil to an evacuated chamber, in which the pressure rise on de-aeration is followed by means of a small McLeod gauge (Vacustat). One instrument is provided with a vibrating stirrer which considerably reduces the time required for de-aeration. An accuracy of ± 3% is attainable.

G. SKIRROW

4256. **Determination of polynuclear aromatics in [medicinal] liquid paraffin.** G. Grimmer, Univ. Hamburg, Germany). *Erdöl u. Kohle*, 1960, **13** (12), 960–963.—The method consists in the preferential dissolution of polynuclear aromatic compounds in nitromethane from a nitromethane-cyclohexane solvent, paper chromatography of the residue from the nitromethane phase, and spectrophotometric determination of the separated components. The polynuclear aromatics are extracted in ≃ 90% yield, and the method is applicable to 0·01 to 0·0001 p.p.m. with an accuracy of ± 5%.

D. DEVOY

4257. **Total analysis of olefinic naphthas by mass spectrometry.** A. J. Frisque, H. M. Grubb, C. H. Ehrhardt and R. W. Vander Haar [Res. and Devel. Dept., Standard Oil Co. (Indiana), Whiting, U.S.A.]. *Anal. Chem.*, 1961, **33** (3), 389–391.—A new method has been developed that combines low- and normal-voltage spectra for the analysis of olefinic naphthas. A CEC Model 21-103 mass spectrometer was modified (full details given) to obtain the required low-ionising and fixed repeller voltages. The method removes the need for chemical separation of hydrocarbon types, and more detailed results are given in a shorter time. It is suggested that other compounds which have a unique mass spectrum for both normal and low-ionising voltages could be analysed in the same way.

R. A. HENDEY

4258. **Determining nitrogen in solid fuels.** W. Radmacher and A. Hoverath. *Glückauf*, 1960, **96**, 1146–1152.—The method described is based on the reductive digestion of the sample with metallic lithium; concurrent determinations of N and S in the same sample are possible. The procedures of Dumas, Kjeldahl and Mantel and Schreiber were used in comparative investigations. Tabulated results indicate the accuracy and applicability of the new method for non-routine analyses. The N in the sample forms a nitride with Li which is decomposed with H_3PO_4, and NH_3 is distilled from the alkaline soln. and determined by titration. Several suggestions for improving the method of Dumas are made. CHEM. ABSTR.

4259. **Rapid complexometric determination of phosphorus in coal.** A. C. Bhattacharyya, B. P. Bhaduri and N. G. Banerjee (Coal Survey Sta., Central Fuel Res. Inst., Raniganj, India). *Analyst*, 1961, **86**, 195–198.—The coal ash (200 mg, or 500 mg if the P content is < 0·2%) is digested with $HClO_4$ and then heated to fuming. To the diluted, filtered and cooled liquid (> 200 ml) are added ammonium tartrate (≃ 0·2 g), citric acid (≃ 0·01 g), 10 ml of aq. triethanolamine soln. (1:1) and 10 ml of 0·1M-EDTA (or nitrilotriacetic acid) and then cold $MgCl_2$-NH_4Cl reagent (prep. described) and drops of aq. NH_3 until the colour of added methyl red changes. The mixture is stirred, and when pptn. of NH_4MgPO_4 begins, aq. NH_3 (5 ml) is added and the stirred liquid is set aside for 2 hr. The collected ppt. is washed with M-aq. NH_3 until a 10-ml portion of the washings becomes blue when 1 drop each of Eriochrome black T indicator (0·2 g in 2 ml of ethanol and 75 ml of triethanolamine) and 0·1M-EDTA are added. The ppt. is dissolved in hot water followed by hot 3N-HCl, the soln. is neutralised with 30% NaOH soln., 10 ml of NH_4NO_3-aq. NH_3 buffer (pH 10) and Eriochrome black T indicator are added, and the liquid is titrated with 0·01M- or 0·005M-EDTA

to the pure blue end-point (1 ml of 0·01M-EDTA ≡ 0·31 mg of P). If the amount of NH_4MgPO_4 pptd. is large, 25 ml of 0·01M-EDTA is added, the mixture is neutralised and adjusted to pH 10 as before, and the excess of EDTA is titrated with standard $MgSO_4$ soln. A. O. JONES

4260. **Mass-spectrometric analysis of asphalt.** R. J. Clerc and M. J. O'Neal, jun. (Houston Res. Lab., Shell Oil Co., P.O. Box 2527, Houston 1, Tex., U.S.A.). *Anal. Chem.*, 1961, **33** (3), 380–382.—A modification of a high-temperature mass-spectrometer enables samples of asphalt and other residual petroleum fractions to be placed within the ionising region. With such an arrangement, mass spectra are obtained from mass 24 to mass 1900. Individual mass peaks are not resolved, but information is provided on the molecular structure of asphalt. C. B. BAINES

4261. **Analysis of surface-active agents. I. Use of ion-exchange resins for separation of mixtures of anionic and non-ionic agents.** A. Arpino and V. de Rosa (Staz. Sperimentale Olii e Grassi, Milan). *Olii Min.*, 1960, **37** (12), 521–527.—The soln. of surface-active agents is passed successively over a cation-exchange resin (H^+ form) and an anion-exchange resin (acetate form); a suitable apparatus and micro-apparatus are described. The former resin converts the anionic agent into the acid, which is retained by the latter resin. The non-ionic agent passes through unchanged and is determined gravimetrically. The anionic agent is eluted with 0·5N-HCl in methanol and then determined gravimetrically. Results for mixtures of Na dodecylbenzenesulphonate and polyoxyethylene glycol octylphenyl ether have been obtained. L. A. O'NEILL

4262. **Determination of the distribution of non-ionic surface-active agents between water and iso-octane.** H. L. Greenwald, E. B. Kice, M. Kenly and J. Kelly (Rohm & Haas Co., 5000 Richmond St., Philadelphia, Pa., U.S.A.). *Anal. Chem.*, 1961, **33** (3), 465–468.—A method is described for the determination of the distribution coefficient as a measure of the relative hydrophilic - lipophilic nature of the surface-active agent. The effect of concn. over a 3000-fold range is investigated for 1,1,3,3-*p*-tetramethylbutylphenoxypolyoxyethylene - ethanol (Kelly and Greenwald, *J. Phys. Chem.*, 1958, **62**, 1096) and results show that the distribution of the agent remains constant for a considerable concn. range below the critical micelle concn. Surface tension and interfacial tension are also measured. C. B. BAINES

4263. **Complexometric titration of inorganic sulphate in synthetic detergents.** H. van Kamp and C. P. M. van den Hondel (N. V. Chem. Fabrick "Andrélon," Bodegraven, Netherlands). *Anal. Chim. Acta*, 1961, **24** (3), 219–223 (in English).—The increase in solubility of $BaSO_4$ in the presence of anionic detergents is prevented by the addition of cetylpyridinium chloride (**I**). *Procedure*—Dissolve the sample (0·02 g of SO_4^{2-}) in 40 ml of H_2O and add a small excess of **I**. Acidify with 0·5N-HCl (2 ml) and add 0·01M-$BaCl_2$ (25 ml). Boil briefly, cool and add 2 ml of *o*-cresolphthalein complexone - naphthol green indicator in dil. aq. NH_3 and 7·5 ml of 25% aq. NH_3. Titrate with 0·01M-EDTA (disodium salt) and add a small excess. Add 100 ml of ethanol and titrate with $BaCl_2$ to a pale-violet colour. P. D. PARR-RICHARD

4264. **Analysis of oil of turpentine by vapour-phase chromatography.** G. Brus, P. Legendre and G. Niolle (Inst. du Pin, Fac. Sci., Bordeaux). *Ann. Falsif.*, 1961, **54**, 142–150.—A Griffin Mark II instrument was used with a glass tube 182 cm long and 1 cm in diam. packed with Celite 545 impregnated with 30% of silicone oil E_{301}, and maintained at 120°. The mobile phase is N flowing at 1 litre per hour and the detector is a katharometer. The major constituents, α-pinene, β-pinene, 3-carene and limonene, in several types of oil of turpentine, have been detected and determined (recoveries from two synthetic mixtures were within ± 3%). Adulteration (*e.g.*, by petroleum derivatives) has been demonstrated, and the botanical origin of some samples has been determined by the presence of specific minor ingredients. R. CLARKE

4265. **Citrus essential oils. I. Evaluation of natural and terpeneless lemon oils.** C. A. Slater [Schweppes (Home) Ltd., The Hyde, London, N.W.9]. *J. Sci. Food Agric.*, 1961, **12** (3), 257–264.—Samples of natural and terpeneless lemon oil have been examined by a combination of absorption and gas chromatography and i.r. spectroscopy. Natural lemon oil contains at least 7 terpenes and 9 sesquiterpenes together with at least 24 oxygenated compounds. It is possible by examination of the oxygenated and hydrocarbon fractions to assess the authenticity and freshness of an oil, but the method does not supersede organoleptic tests. I. DICKINSON

4266. **Reductimetric determination of hydroxytriphenylmethane dyes with vanadium(II) sulphate.** M. Matrka and Z. Ságner (Res. Inst. Org. Synth., Pardubice-Rybitví, Czechoslovakia). *Chem. Prům ysl*, 1961, **11** (3), 135.—*Procedure*—Dissolve the sample (0·3 g) in ethanol (50 ml), dilute with H_2O (100 ml), add conc. H_2SO_4 (5 ml), heat at 50°, add 0·1N-VSO_4 (25 ml) and, after 1 min., cool and titrate with 0·1N-$(NH_4)_2SO_4.Fe_2(SO_4)_3$, with Safranine T (C.I. Basic Red 2) soln. (0·2%) as indicator, or potentiometrically. The procedure is carried out in a nitrogen atmosphere. The following dyes were determined—aurine, Eriochrome azurol (C.I. Mordant Blue 1), Chrome blue R (C.I. Mordant Blue 42), Chromoxane brown 5R (C.I. Mordant Brown 26) and Naphthochrome azurine B (C.I. Mordant Blue 28). J. ZÝKA

4267. **Colorimetric method for determining the reducing carbonyl groups in cellulose.** O. Szabolcs. *Papier, Darmstadt*, 1961, **15** (2), 41–44 (in German).—The reducing groups in cellulose were determined by colorimetry of the red dye (triphenylformazan) formed from 2,3,5-triphenyltetrazolium chloride by the action of reducing agents in alkaline medium, whereby the quantity of formazan formed is proportional to the reducing agent present. The dye is insoluble in water, but easily soluble in organic solvents. The determination can be carried out in 15 min. with an accuracy of ± 1%. The method is generally applicable, even in cases where the conventional methods cannot be used. The extinction value of a 10-mg sample was expressed as "formazan number" and compared with the conventional copper-number and iodine-value methods; only the latter gives as good results as the formazan method. When calculating the degree of polymerisation of cellulose samples from the percentages of reducing carbonyl groups, it was found that in most celluloses the reducing-group

content is greater than that corresponding to the viscometrically determined degree of polymerisation. SHIRLEY INST. SUMM. CURR. LIT.

4268. **Ebulliometric apparatus for studying number-average molecular weights of polymers.** C. A. Glover and R. R. Stanley (Res. Lab., Tennessee Eastman Co., Kingsport, U.S.A.). *Anal. Chem.*, 1961, **33** (3), 447–450.- The apparatus described, simple in design and operation, is a combination of a Menzies - Wright ebulliometer and an 80-junction, copper - constantan thermocouple which serves as the temperature-sensing element. The thermopile output is fed through a stabilised d.c. amplifier to a strip-chart recorder, where it is continuously recorded. A polymer molecular weight can be calculated in 4 hr. with no more than 1 hr. of actual operator time. C. B. BAINES

4269. **Separate determination of pyridine and nitrile nitrogen in vinyl cyanide - 5-vinyl-2-picoline copolymer.** E. A. Emelin, G. P. Svistunova and Ya. A. Tsarfin (Vladimir Sci. Res. Inst. of Synthetic Resins). *Zavod. Lab.*, 1961, **27** (3), 283–285.—The 5-vinyl-2-picoline in the copolymer is determined by the method of Streuli (*Anal. Abstr.*, 1956, **3**, 1081). The nitrile N is determined by hydrolysis with 40% KOH soln. and volumetric determination of the NH_3 after absorption in 0·1N-HCl. G. S. SMITH

4270. **Hygienic evaluation of plastic materials. I. Determination of formaldehyde in aminoplasts and phenoplasts.** L. Służewska and H. Piekacz (Dept. of Anal. of Food and Objects of Common Use, State Inst. of Hygiene, Warsaw, Poland). *Roczn. Zakł. Hig., Warsaw*, 1960, **11** (6), 557–566.—Two methods (iodimetric and colorimetric) were compared, the latter being preferred. *Procedure*—Fill the vessel to be tested with boiling water, cover and set aside at 20° for 2 hr. To 1 ml of the aq. extract (≃ 1·25 to 25 μg of formaldehyde) add 5 ml of 0·25% chromotropic acid soln. in 72% H_2SO_4, mix, place in a water bath for 10 min. at 60° and compare the colour with standards prepared by the same procedure with formaldehyde soln. B. K.

4271. **Determination of processing aids (plasticisers) in cellulose hydrate film.** E. Schröder (Inst. f. Chem. Tech. Plaste, Leipzig). *Plaste u. Kautsch.*, 1960, **7** (4), 167–168.—The film is extracted by boiling with water and on one portion of the extract the glycerol is determined volumetrically by oxidation with HIO_4. Another portion is oxidised with alkaline $KMnO_4$ and the polyoxyethylene glycol wax content is determined volumetrically, making allowance for the glycerol present. Qualitatively, the wax may be detected by treating the film with a few drops of conc. H_2SO_4 and absorbing the vapours in a satd. $HgCl_2$ soln., when a polyoxyethylene glycol gives a colourless cryst. ppt. Glycerol is best detected by a suitable colour test after extraction with acetone. L. A. O'NEILL

4272. **Identification of antioxidants of rubber by paper chromatography.** J. P. Varma, N. P. Suryanarayana and A. K. Sircar (Indian Rubber Manufacturers' Res. Ass., Nat. Chem. Lab., Poona). *J. Sci. Ind. Res., India, D*, 1961, **20** (2), 79–81.—The work described is an extension of that of Zijp (*Anal. Abstr.*, 1957, **4**, 2692). The vulcanised test sample containing a phenolic or amine-type antioxidant is cut into small pieces (5 mesh) and extracted with acetone for 2 hr. The dried extract is dissolved in 15 ml of ethanol, 3 drops of 4N-aq. NH_3 and 3 drops of 20% $SrCl_2$ soln. are added, the ppt. formed is filtered off and the filtrate is concentrated to 1 ml. Chromatography is carried out on fully acetylated Whatman No. 1 paper. The R_F values of the antioxidants (*e.g.*, *N*-phenyl-2-naphthylamine and 2-mercaptobenzimidazole) in the original sample and in the extract from the vulcanised sample with different mobile phases, and the colours of the spots obtained with locating agents, are tabulated and discussed. B. B. BAUMINGER

4273. **The simple micro scale differential thermal analysis of explosives.** R. N. Rogers (Los Alamos Sci. Lab., New Mexico, U.S.A.). *Microchem. J.*, 1961, **5** (1), 91–99.—The design and construction are described of a simple cell, capable of yielding sharp temp. resolution with samples smaller than 10 mg, for the routine differential thermal analysis (DTA) of high explosives and explosive compositions. The two compartments of the cell are arranged axially and each contains a simple thermocouple, which can readily be replaced. A simple, expendable tube-furnace, capable of providing consistent heating rates, is also described. The DTA and pyrolysis curves of several common explosives, which were run at a heating rate of 11° per min., have been reproduced. I. A. SIMPSON

See also Abstracts—**4029**, Detection of elements in org. comp. **4031**, Analysis of petrol. **4035**, Determination of dihydroxymaleic acid. **4037**, Determination of K rhodizonate and 1-nitroso-2-naphthol. **4043**, Separation by ligand exchange. **4089**, Hg^{II} in presence of organic Hg. **4093**, Detection of poly(vinyl alcohol). **4146**, S in aq. soln. from petroleum. **4348**, Determination of maltotriose. **4350**, Fluoride in gelatin. **4355**, Purity of food dyes. **4374**. Identification of aliphatic amines. **4401**, M. p. of polymers. **4405**, Determination of 5-hydroxymethyl-2-furaldehyde and laevulic acid.

4.—BIOCHEMISTRY

INCLUDING DRUGS, FOOD, SANITATION, AGRICULTURE

Biological fluids, animal and vegetable tissues

4274. **Influence of various deproteinising agents on the determination of electrolytes by flame photometry. I. Influence of tungstic acid, copper tungstate and zinc hydroxide on the determination of potassium in blood serum.** M. E. Cobe de Celis, A. Martin and B. Pacheco (Univ. Nac. de Cordoba, Argentina). *Rev. Asoc. Bioquim. Argentina*, 1960, **25**, 95–102.—The influence of different deproteinising agents in the flame-photometric determination of K in blood serum has been studied. Tungstic acid, copper tungstate and $ZnSO_4$ - $Ba(OH)_2$ gave average losses of 6·7, 5 and 70%, respectively. Even greater losses occurred with aq. potassium soln. The best results were given by $ZnSO_4$ - NaOH, which gave an average positive error of 3% with serum and an almost theoretical recovery with the aq. soln. L. A. O'NEILL

4275. **X-ray spectrometric determination of strontium in human serum and bone.** S. Natelson and B. Sheid (Roosevelt Hospital, New York, U.S.A.). *Anal. Chem.*, 1961, **33** (3), 396–401.—Approx. 200 mg of the ashed sample is dissolved in 2N-HCl (0·1 ml) and, after dilution to 1 ml with H_2O, the soln. is evaporated (10 to 20 min.) in a ring-oven apparatus (illustrated) so that the residue is retained uniformly in a confined area on pre-treated Whatman 3MM paper. The concn. of Sr in the spot is then determined by the X-ray spectrometric procedure described previously (Natelson *et al.*, *Anal. Abstr.*, 1960, **7**, 4901), the K_α line of Sr, a LiF crystal, and a narrow band-pass for the pulse-height analyser being used. The counts per sec. are compared with those for a series of standards (3 to 25 μg of Sr per 25 μl). To minimise the high background of the K_α line, the blank is prepared with an identical matrix, except that the Sr has been replaced by Ca (by ion exchange). Optimum operating conditions are discussed. Human serum has a Ca to Sr ratio of $\simeq$ 390, with concn. of Sr ranging from 16 to 31 μg per 100 ml; for six analyses from normal pools the mean was 25·6 μg with a standard deviation of 1·02 μg. W. J. Baker

4276. **Spectrochemical determination of yttrium in biological materials.** C. L. Grant (State Univ., New Brunswick, N.J., U.S.A.). *Anal. Chem.*, 1961, **33** (3), 401–404.—The sample (1 to 2 g, 0·05 to 1000 p.p.m. of Y) is pre-treated so as to be in soln. in 100 ml of 0·1N-HCl. This soln. is then passed through a column (22 cm × 1·54 sq. cm) of Amberlite IR-120 (Cl^- form, 16 to 50 mesh) at a rate of $\simeq$ 3 ml per min. and the Y is eluted from the column at 50° with 6N-HCl (1200 ml). The eluate is concentrated to $\simeq$ 5 ml, evaporated almost to dryness with 6N-HCl, and taken up in 2N-HCl (1 ml) containing Ca (4 mg) and La (200 μg); the vol. is made up to 2 ml with H_2O. Aliquots (0·10 ml) of this final soln. are submitted to high-voltage spark-discharge between graphite electrodes, and the concn. of Y is determined from the intensities of the lines of Y 3242·28 and La 3245·12 A, in comparison with the calibration curves for 0·05 to 5 μg of Y per 0·10 ml. The procedure for preparing the final soln. is flexible, but the vol. sparked must always contain 0·05 to 5 μg of Y, 10 μg of La (internal standard) and 200 μg of Ca (matrix). The recovery of Y is $\simeq$ 94% for concn. of 2 to 35 p.p.m. in the ash, and the coeff. of variation is $\pm$ 6 (4 analyses). The method is specially suitable for the analysis of bone-tissue and egg shells. W. J. Baker

4277. **Urinalysis for curium by electro-deposition.** I. Dupzyke and M. W. Biggs (Lawrence Radiation Lab., California Univ., Livermore, U.S.A.). *U.S. Atomic Energy Comm.*, Rep. UCRL-6168, 1960. 18 pp.—The urine is wet-ashed, and the Cm is co-pptd. with $BiPO_4$, then with LaF_3, and finally with $La(OH)_3$. The Cm is separated from the lanthanum carrier with Dowex-50 colloidal ion-exchange resin. Electro-deposition on a stainless-steel or platinum disc gives a uniform film suitable for pulse-height analysis or low-background proportional counting. Final analysis of weak samples is made by radio-autography. Curium recoveries of $\simeq$ 45% are obtained. Quantities of the order of 0·2 disintegration per min. can be detected by this method. Nucl. Sci. Abstr.

4278. **Spectrophotometric determination of germanium in biological materials.** G. Rosenfeld (Naval Med. Res. Unit No. 1, Univ. Calif., Berkeley, U.S.A.). *Anal. Biochem.*, 1960, **1** (6), 469–477.—The sample of biological material (5 g) is digested with conc. H_2SO_4 (10 ml) and conc. HNO_3 (15 ml) in a 125-ml Erlenmeyer flask, oxidising conditions being maintained by further additions of HNO_3 (5 ml) if necessary. When digestion is complete, heating is continued until fumes of SO_3 are evolved. The digest is transferred quantitatively to a distillation flask, rinsing twice with water (4 ml), and heated again until fumes of SO_3 are evolved to ensure complete removal of nitrogen oxides. To the cooled soln. is added HCl (1:3) (5 ml) through a delivery tube and distillation is carried out for 10 min. at a temp. $\geqslant$ 120° whilst passing air at a rate of about 10 bubbles per min. The distillate is condensed in a water-cooled condenser, the tip of which extends to the bottom of a receiver cooled in cracked ice and containing water (4 ml) and Na acetate soln. (100 g of Na acetate trihydrate in 100 ml of water) (4 ml). The condenser tube is rinsed with water (13 ml) directly into the receiver, followed by 5·31% $(NH_4)_6Mo_7O_{24}.4H_2O$ soln. (2 ml), 2·1% $(NH_4)_2SO_4.FeSO_4.6H_2O$ soln. in 0·02N-H_2SO_4 (1 ml), and water to make the vol. up to 25 ml. The extinction is read at 880 mμ after 30 min. A standard germanium soln. containing 1000 μg per ml is prepared by dissolving 1·4408 g of GeO_2 in 500 ml of water containing 25 ml of N-NaOH, neutralising with HCl and making up to 1 litre with water. A reference curve is prepared by adding known amounts of Ge to Na acetate soln. (4 ml) and HCl (1:1) (1·75 ml), diluting to 21 ml with water and developing the colour as described above. A blank is prepared similarly, but omitting the Ge. Beer's law is obeyed for amounts of Ge between 2 and 50 μg, but amounts up to 500 μg can be determined even after colour development by dilution with a soln. prepared exactly as the reference-curve blank. The use of this method eliminates interference due to arsenic, silicic and phosphoric acids. R. A. Brenan

4279. **Determination of [elementary] phosphorus in biological material.** W. T. Oliver and H. S. Funnell (Ontario Veterinary Coll., Guelph, Canada). *Anal. Chem.*, 1961, **33** (3), 434–435.—A mixture of the tissue (10 g) with 1% tartaric acid (10 ml) is heated in N and the evolved P is collected on $HgBr_2$ in an absorption tube, from which it is eluted with 0·003N-iodine (8 ml). The H_3PO_4 is then determined colorimetrically at 720 mμ by the hetero-poly-blue method. From 1 to 54 μg of P can be determined to within $\simeq$ 0·2 μg. W. J. Baker

4280. **Determination of arsenic and antimony in biological material.** L. A. Dal Cortivo, M. Cefola and C. J. Umberger (Fordham Univ., New York, U.S.A.). *Anal. Biochem.*, 1960, **1** (6), 491–497.—The biological material (100 ml of urine, 10 to 20 ml of blood, or 10 to 20 g of tissue or hair) is first digested with conc. H_2SO_4 and conc. HNO_3 in the apparatus described by Bethge (*Anal. Abstr.*, 1954, **1**, 1727). All remaining traces of oxidants are removed by adding water (10 ml) and oxalic acid (0·5 g) to the clear digest and heating until fumes of SO_3 are evolved. After cooling, the flask is removed from the digestion unit and 5% $CdSO_4$ soln. (0·5 ml), 25% H_2SO_4 (50 ml) and zinc metal (10 g) are added. The flask is immediately attached to a Pb acetate scrubber and a specially designed absorbing column charged with Ag diethyldithiocarbamate - pyridine reagent (2 ml), prepared as

follows—$AgNO_3$ soln. (1·7 g in 100 ml of water) is added slowly, with stirring, to Na diethyldithiocarbamate soln. (2·3 g in 100 ml of water); the yellow ppt. of Ag diethyldithiocarbamate is filtered off, washed with water, dried in a vacuum desiccator and dissolved in anhyd. pyridine to give a soln. containing 5 mg per ml. After 1 hr. the contents of the absorber are transferred to a 5-ml flask, the absorber is washed down with pyridine (2 ml), and the volume is made up with pyridine. The extinction is read at 540 mμ for As or at 510 mμ for Sb against a pyridine blank, and the results are calculated from a previously prepared reference curve. The results of some recovery experiments are reported. R. A. BRENAN

4281. **Polarographic characterisation and microdetermination of arsenic and antimony in biological media after isolation as xanthates.** L. Vignoli, B. Cristau and F. Gouezo (Lab. de Pharm. Chim. et de Toxicol., Fac. de Méd. et de Pharm., Boulevard d'Alès, Marseille). *Ann. Falsif.*, 1961, **54**, 132–141.—After initial destruction of organic matter with HNO_3 and H_2SO_4, and reduction to As^{3+} and Sb^{3+} with KI, the xanthates are formed and extracted by shaking the soln. vigorously with a fresh soln. of sodium ethylxanthate in CCl_4. The solvent is evaporated (the last few ml on a water bath) and the xanthates are decomposed with a mixture of H_2SO_4, $HClO_4$ and HNO_3 (7:2:1). The As and Sb are then reduced to their hydrides, which are absorbed on paper impregnated with $AgNO_3$ and extracted therefrom with a soln. of HCl and tartaric acid (1 mole of each per litre). The extract is then polarographed ($E_{\frac{1}{2}}$ for Sb = −0·19 V; for As = −0·43 V). The method is not recommended for < μg of As or < 25 μg of Sb; for 10 to 125 μg of As and 25 to 100 μg of Sb, the recovery from four mixtures of varied proportions was 87 ± 4%. R. CLARKE

4282. **Indirect flame-photometric determination of total sulphur in biological materials.** W. M. Shaw (Univ. of Tennessee Agric. Exp. Sta., Knoxville, U.S.A). *J. Agric. Food Chem.*, 1961, **9** (1), 18–21.—Plant or animal tissue (1 g) or an organic sulphur compound (0·1 g) is digested with 70% HNO_3 - 70% $HClO_4$ (1:1) (10 ml). After complete removal of the acids and dissolution of the residue in dil. HCl, the SO_4^{2-} are pptd. by addition of a known vol. of 0·0625N-$BaCl_2$, phosphate if present is pptd. by an acetate - $FeCl_3$ treatment, and the combined filtrates are examined flame-photometrically at 515 mμ to determine the Ba. For materials low in Ca, $CaCl_2$ is added during the digestion to fix the S; $CaCl_2$ is added (with KCl and $MgCl_2$) to the calibration standards to compensate for co-pptn. and spectral errors due to Ca. Results comparable in accuracy with gravimetric results were obtained on samples of a wide range of materials, including wheat straw, blood meal, casein and methionine, containing from < 1 mg to 26 mg of S. C. L. HINTON

4283. **Spectrophotometric determination of iron in blood with dianisidine (3,3′-dimethoxybenzidine).** C. Vassiliades and G. Manoussakis (Lab. Chim. Min., Univ. Thessaloniki, Greece). *Bull. Soc. Chim. France*, 1961, (3), 582–583.—The sample is evaporated to dryness and heated at 550° for 2 hr. with a few drops of H_2O_2 soln. After cooling, 1 or 2 more drops of H_2O_2 soln. are added and evaporated. The residue is dissolved in dil. HCl. Wet oxidation is less satisfactory, but is also described. A portion of the soln., to which HNO_3 and H_2O have been added, is adjusted to pH 2·5 to 2·6 and an ethanolic soln. of dianisidine is added. The extinction is measured at 450 mμ after 15 min. and the measurement is repeated until the extinction has reached a max. The results are in good agreement with those obtained with 1,10-phenanthroline. The method is also applicable to the determination of Fe^{3+} in the presence of Fe^{2+}. G. BURGER

4284. **Application of neutron-activation analysis to the micro-analysis of gold-containing pharmaceuticals in biological materials.** J. P. Vacik and J. E. Christian (Bionucleonics Dept., Sch. of Pharm., Purdue Univ., Lafayette, Ind., U.S.A.). *J. Pharm. Sci.*, 1961, **50** (3), 225–227.—Irradiate the crude sample (*e.g.*, 0·5 ml of liver-tissue homogenate containing 5 to 60 μg of Au), contained in a polyethylene tube in a Plexiglas holder, with thermal neutrons at a flux of 2×10^9 per sq. cm per sec. for 1 hr., set aside for 12 hr. and measure the activity at the 0·411-MeV peak of ^{198}Au with a γ-ray scintillation spectrometer. Use a gold chloride standard soln. to correct for variations in flux between holders and between bombardments. A. R. ROGERS

4285. **Sampling technique for the infra-red analysis of volatile organic materials in animal tissues.** D. N. Robertson and D. S. Erley (Dow Chemical Co., Midland, Michigan, U.S.A.). *Anal. Biochem.*, 1961, **2** (1), 45–49.—Anaesthetics (*e.g.*, ethyl ether and $CHCl_3$) in animal tissues are extracted with CS_2 and, after distillation of the extract, are analysed by infra-red spectrophotometry. An all-glass apparatus that simplifies the extraction and distillation is described and illustrated. *Procedure*—Tissue samples (0·5 to 2·5 g) are extracted with CS_2 (5 ml) for several hours. The extract is distilled directly from the tissue at 75° for 10 to 15 min., and an aliquot of the distillate is scanned in a double-beam infra-red spectrometer. The extinction is measured and the concn. of anaesthetic is obtained by the use of a standard curve. The accuracy of the method is ± 10%. E. C. BUTTERWORTH

4286. **Quantitative determination of sugars by rapid horizontal paper chromatography.** J. B. Himes, L. D. Metcalfe and H. Ralston (Armour Industrial Chem. Co., McCook, Ill., U.S.A.). *Anal. Chem.*, 1961, **33** (3), 364–366.—High-temperature paper chromatography is used to separate and determine mixed sugars in fermenting liquors. The chromatographic tank is that described by Himes and Metcalfe (*Ibid.*, 1959, **31**, 1192) and the solvent is prepared by mixing 25 ml of propionic acid and 75 ml of ethyl methyl ketone, and then adding 30 ml of H_2O. *Procedure*—Samples (1 or 2 μl, containing 10 to 20 mg of each sugar per ml) and standard sugar soln. are spotted on to Whatman No. 1 paper (8 in. × 11·5 in.) and dried. The paper is then placed in the chromatographic chamber (pre-heated for 1 hr. at 60°), the chamber is sealed, and the solvent is added. The chamber is maintained at 60° for 2 hr., then the paper is removed and air-dried for 30 min. The spots are revealed with aniline phosphate soln. (mix 1 vol. of 2N-aniline in n-butanol with 2 vol. of 2N-H_3PO_4 in n-butanol, and filter). The chromatogram is air-dried for 30 min., then heated at 80° to 85° for 30 min., and the coloured spots are

measured with a densitometer at 445 mμ. Results on known mixtures were, in general, within ± 2% of the theoretical. R. A. HENDEY

4287. **Fluorimetric method for the determination of 2-deoxy-D-glucose.** M. Blecher and B. Dvorkin (Dept. of Biochem., Albert Einstein Coll. of Med., Yeshiva Univ., New York). *Anal. Biochem.*, 1961, **2** (1), 30–38.—2-Deoxy-D-glucose is condensed with 3,5-diaminobenzoic acid dihydrochloride and the resulting product [probably 7-amino-2-(2,3-dihydroxypropoxy)quinoline-5-carboxylic acid] is determined fluorimetrically. The fluorescence is proportional to concn. of deoxy-D-glucose between 2·8 and 125 mμmoles per ml. Tissues containing high concn. of deoxyribose give zero blanks, and high concn. of glucose do not interfere.
E. C. BUTTERWORTH

4288. **Estimation of lactose in rat mammary-gland suspensions.** T. F. Slater (Dept. of Biochem., Univ. Coll., London). *Biochem. J.*, 1961, **78** (3), 668–672.—The chloramine-T and orcinol methods for the determination of lactose in suspensions of rat mammary gland are compared during late pregnancy and during lactation. The chloramine-T method gives higher values than the orcinol procedure during lactation, whilst in late pregnancy the values are 3·7 times as high. Under the conditions of the lactose assay, any protein that comes through the pptn. stage, free amino-acids and free mercapto-groups all react with the chloramine T, and produce an apparent lactose titre. The results obtained with the orcinol method in late pregnancy are possibly due to the presence of carbohydrates other than lactose.
J. N. ASHLEY

4289. **Determination of ascorbic acid in blood.** E. R. H. Lench and G. T. Lewis (Dept. of Biochem., Univ., Miami, Fla., U.S.A.). *Chemist Analyst*, 1961, **50** (1), 18–19.—The method of Roe and Kuether (*J. Biol. Chem.*, 1943, **147**, 399) is modified by using 2,6-dichlorophenolindophenol (**I**) as oxidant instead of active carbon, adjusting concn. to give greater extinction values and adding HNO_3 (1:1) in the warm instead of conc. H_2SO_4 in the cold. *Procedure*—The blood (5 ml) is deproteinised by adding it to 5 ml of 12% trichloroacetic acid, dropwise with agitation, setting aside for 10 min. and centrifuging. Two 2-ml portions are taken, 1 drop of a 0·2% aq. soln. of **I** is added to each and, after 4 min., 4 drops of 10% aq. thiourea soln. One tube is retained as a blank, and 6 drops of 2,4-dinitrophenylhydrazine soln. [4% in H_2SO_4 (1:3)] are added to the assay soln. The tube is capped and warmed in a water bath at 37° for exactly 3 hr., then 4 ml of HNO_3 (1:1) is rapidly added and mixed and the soln. is set aside for 30 min. The blank soln. is treated with 4 ml of HNO_3 (1:1) and 6 drops of dinitrophenylhydrazine soln. The extinction of each soln. is measured against H_2O with a green filter. Standards are best prepared by the addition of ascorbic acid to 5-ml aliquots of aged blood. The results show good reproducibility, and agree satisfactorily with those by other methods. J. H. WATON

4290. **Rapid procedure for the determination of adrenal ascorbic acid. Application of the Sullivan and Clarke method to tissues.** R. P. Maickel (Nat. Heart Inst., Bethesda, Md., U.S.A.). *Anal. Biochem.*, 1960, **1** (6), 498–501.—The method is based on the measurement of the reduction of Fe^{3+} at pH 1 to 2 in the presence of excess of PO_4^{3-} by coupling the Fe^{3+} produced with 2,2′-bipyridyl. Adrenal tissue, either fresh, or frozen and stored at − 4° (10 to 100 mg), is homogenised in 200 vol. of cold 5% trichloroacetic acid soln. in an all-glass homogeniser and centrifuged at 4° for 5 min. at 9000 *g*. To an aliquot of the supernatant liquid (1 ml containing 10 to 40 μg of ascorbic acid) are added 85% H_3PO_4 (0·3 ml), 0·5% aq. 2,2′-bipyridyl soln. (5 ml) and 1% $FeCl_3$ soln. (1 ml), mixing after each addition. After setting aside the soln. for 10 min. the extinction is read at 525 mμ against water. A standard soln. containing 25 μg of ascorbic acid per ml in 5% trichloroacetic acid is treated similarly. R. A. BRENAN

4291. **Identification of hydroxamic acids by gas chromatography of isocyanate derivatives.** P. R. Vagelos, W. J. A. Vanden Heuvel and M. G. Horning (Lab. of Cellular Physiol. and Metabolism, Nat. Heart Inst., Bethesda, Md., U.S.A.). *Anal. Biochem.*, 1961, **2** (1), 50–58.—Hydroxamic acids are quantitatively acetylated by treatment with excess of acetic anhydride and pyridine, and the reaction mixture is applied directly to the gas-chromatographic column without isolation or purification of the esters formed. The flash heater of the column converts the esters quantitatively into isocyanates, which are readily separated. The method can be used for both qualitative and quantitative analysis of mixtures of long-chain acyl coenzyme-A compounds.
E. C. BUTTERWORTH

4292. **Micro-analytical determination of urinary aromatic acids by gas chromatography.** C. C. Sweeley and C. M. Williams (Dept. of Biochem. and Nutrition, Graduate School of Public Health, Univ. Pittsburgh, Pa., U.S.A.). *Anal. Biochem.*, 1961, **2** (1), 83–86.—Two columns, U-shaped, with a total length of 6 ft. and internal diam. 0·25 in., are used. A polar column containing 10% (w/w) of ethanediol - adipic acid polyester coated on 60 to 80-mesh siliconised Chromosorb W (*cf.* Horning *et al.*, *Anal. Abstr.*, 1960, **7**, 816) is operated at 206° with an argon inlet pressure of 15 lb per sq. in. A non-polar column, containing 3% (w/w) of silicone gum on 80 to 100-mesh Chromosorb W, is operated at 191° with an argon inlet pressure of 18 lb per sq. in. Homovanillic acid, *p*-hydroxyphenylacetic acid and hippuric acid are measured on the polar column, while 4-hydroxy-3-methoxymandelic acid, indol-3-ylacetic acid and 5-hydroxyindol-3-ylacetic acid are determined more accurately on the non-polar column. The aromatic acids isolated from urine by the method of Armstrong *et al.* (*J. Biol. Chem.*, 1956, **218**, 293) are converted into their methyl esters before analysis. With an instrument equipped with argon ionisation detectors (*cf.* Lovelock, *Anal. Abstr.*, 1958, **5**, 3208) it is possible to obtain complete analyses with 50 to 100-μg loads corresponding to a vol. of urine containing 0·2 to 0·5 mg of creatinine.
E. C. BUTTERWORTH

4293. **Fluorimetric assay for gibberellic acid.** R. J. Theriault, W. C. Friedland, M. H. Peterson and J. C. Sylvester (Dept. of Microbial Physiol., Abbott Lab., N. Chicago, Ill., U.S.A.). *J. Agric. Food Chem.*, 1961, **9** (1), 21–23.—The method depends on the strong fluorescence in u.v. light shown by gibberellic acid (**I**) after treatment with cold conc. H_2SO_4. Gibberellin A_1 shows practically no fluorescence under these conditions. Samples

dissolved in water or a water-miscible solvent are filtered if not clear, and diluted to $\simeq 4$ μg per ml with 0·5% KH_2PO_4 soln. (adjusted to pH 3·0 with H_3PO_4), and 1 ml of diluted sample is extracted with ethyl acetate (3 × 3 ml). The combined extracts are evaporated to dryness in a 10-ml flask, 1 ml of water is added and the soln. is rapidly frozen in an isopropyl alcohol - solid CO_2 bath, and the flask is then placed in an ice bath. Conc. H_2SO_4 (4 ml) at $\simeq 1°$ is added rapidly from a syringe, and the flask is swirled to ensure complete mixing and left in the bath for 10 min. Cool (10° to 15°) 5N-H_2SO_4 (4 ml) is then added, the flask is again swirled and left in the bath for a further 5 min. The soln. is made up to vol. with cool 5N-H_2SO_4, and examined in a spectrophotofluorimeter or a photofluorimeter with suitable filters. The max. activating wavelength is 405 mμ and the max. fluorescence wavelength 455 mμ. A standard curve is prepared from dilutions (1 to 8 μg per ml) of a stock soln. (100 μg per ml) of **I** in water. Samples dissolved in water-immiscible solvents are diluted to $\simeq 4$ μg per ml with the same solvent, 1 ml of the soln. is evaporated to dryness, and the residue is dissolved in 1 ml of water. The method does not correct for gibberellenic acid, which has been stated to interfere. C. L. HINTON

4294. **An enzymic spectrophotometric method for the determination of homogentisic acid in plasma and urine.** J. E. Seegmiller, V. G. Zannoni, L. Laster and B. N. La Du (Nat. Inst. of Arthritis and Metabol. Dis., Bethesda, Md., U.S.A.). *J. Biol. Chem.*, 1961, **236** (3), 774–777.—The method, by which as little as 1 μg of the acid can be detected, is based on the enzymic conversion of homogentisic acid into maleylacetoacetic acid by means of a partially purified homogentisic acid oxidase, and the extinction of the reaction mixture is measured at 330 mμ. J. N. ASHLEY

4295. **Polarographic determination of mesobilirubin in the presence of bilirubin.** B. Tvaroha (I Med. Klinik, Charles' Univ., Prague, Czechoslovakia). *Naturwissenschaften*, 1961, **48** (4), 99 (in German).—A soln. of the two compounds in 0·1N-NaOH shows two maxima, one at $E_{\frac{1}{2}} = -1{\cdot}48$ V *vs.* the S.C.E. [bilirubin (**I**)] and the other at $E_{\frac{1}{2}} = -1{\cdot}62$ V *vs.* the S.C.E. [mesobilirubin (**II**)]. The height has a direct relationship with the concn., and determination of **II** can be made in the presence of a tenfold concn. of **I** with satisfactory accuracy. H. F. W. KIRKPATRICK

4296. **New chromatographic method for the determination of thiamine and its mono-, di- and tri-phosphates in animal tissues.** G. Rindi and L. de Giuseppe (Inst. of Human Physiol., Univ. of Pavia, Italy). *Biochem. J.*, 1961, **78** (3), 602–606.—The tissue is extracted and deproteinised by homogenisation in 5% (v/v) trichloroacetic acid. The extract is adjusted to pH 6·7 to 6·8, adsorbed on a charcoal column, and then eluted with 10% (v/v) n-propanol. The eluate, which has been concentrated *in vacuo*, is applied to a column of Dowex 1-X8 (acetate form), which retains thiamine diphosphate and triphosphate, and allows free thiamine and the monophosphate to flow through. The contents of these in the percolate and the combined washings are then determined. The diphosphate is eluted from the column with 0·02M-Na acetate in 0·04M-acetic acid, and the triphosphate is eluted with M-acetate buffer, pH 4·5. Each phosphate is then determined in the eluates. Thiamine is determined by the thiochrome method, and the esters are hydrolysed to thiamine by acid phosphatase before the determination. Excluding the overnight incubation with phosphatase, the time needed for the whole process is about 12 hr. The method gives a mean thiamine recovery of 95% and the results are reproducible. J. N. ASHLEY

4297. **Colorimetric determination of glucosamine in the presence of its 3-(*O*-methyl) derivative.** M. Pesez, J. Bartos and A. Sezerat (Centre de Rech. Roussel-Uclaf, Paris). *Bull. Soc. Chim. France*, 1961, (3), 567–568.—Three modifications of the procedure of Elson and Morgan (*Biochem. J.*, 1933, **27**, 1824) are described. To determine glucosamine and the derivative together, the sample is heated with a 1% soln. of acetylacetone in N-Na_2CO_3 and cooled to 0°. The colour is developed by heating this soln. with xanthhydrol or flavylium perchlorate. Each of these reagents is used as a 0·1% soln. in acetic acid containing 1% of conc. HCl. To determine glucosamine in the presence of the derivative, the sample is heated in alkaline soln. with a 5% soln. of phenylacetone in a mixture of ethanediol and water (3:1) and cooled to 0°. The colour is developed at room temp. by the addition of HCl, ethanol and a 2% soln. of *p*-dimethylaminobenzaldehyde in 5N-HCl. G. BURGER

4298. **Method for separating neutral amino-acids from neutral oligopeptides.** P. R. Carnegie (Rowett Res. Inst., Bucksburn, Aberdeen, Scotland). *Biochem. J.*, 1961, **78** (4), 687–691.—Monocarboxylic mono-amino-acids are separated from their dipeptides on a column of Dowex 1-X8 (Cl^- form), and are eluted with ammonium acetate buffer (pH 8·65). The peptides are retained on the resin and are subsequently eluted with acetic acid. Carbon dioxide interferes with the separations and this interference may be due to the formation of ureido-acids. A semi-quant. technique with two-dimensional chromatography - ionophoresis on filter-paper is described for assessment of the results of the separation. J. N. ASHLEY

4299. **Separation of amino-acid mixtures on sulphonated polystyrene resin-loaded papers.** C. S. Knight (Whatman Res. Lab., Springfield Mill, Maidstone, Kent, England). *Nature*, 1960, **188**, 739–740.—Separations of amino-acids have been carried out on paper containing Zeo-Karb 225 (*WR* 1·5–2·0) resin and its resolving powers compared qualitatively with those of the resin in column form. Some differences in sequence on the two forms of the resin occur. With the exception of these differences the high resolution of the column technique is matched by that of the paper and, because the latter can be achieved without elution, the time required is considerably reduced. (*Cf. Anal. Abstr.*, 1959, **6**, 4214; 1960, **7**, 3428.) N. E.

4300. **Gas chromatography of the *N*-trifluoroacetylmethyl esters of the amino-acids.** H. A. Saroff and A. Karmen (Nat. Inst. of Arthritis and Metabolic Diseases, Bethesda, Md., U.S.A.). *Anal. Biochem.*, 1960, **1** (4–5), 344–350.—The *N*-trifluoroacetylmethyl esters of 14 common amino-acids gave single peaks on polyester columns. Improved yields of the derivatives were obtained by the use of sulphonated polystyrene resin (H^+ form) as a catalyst for the formation of the methyl ester.

The advantages of gas chromatography are speed and sensitivity; 10^{-3} to 10^{-4} μmole of amino-acid can be detected. F. POWELL

4301. **Amperometric determination of free cystamine in biological liquids.** B. Mondovì, M. T. Costa and G. Ferro-Luzzi (Ist. di Chim. Biol., Univ. Roma, Italy). *Ital. J. Biochem.*, 1961, **10** (1), 42–49.—The method depends on the separation of cystamine from biological materials by ion exchange, reduction of the disulphide group to mercapto with $NaHSO_3$, and amperometric titration with a rotating platinum electrode (1 cm long, 150 r.p.m.). *Procedure*—Transfer the sample (≃ 1 mg of cystamine) to a column (2 cm × 10 cm) of Dowex 2 (OH^- form, 80 to 100 mesh), and elute with water (300 ml). Acidify the eluate with 2N-HCl (15 ml) and pass through a similar column packed with Dowex 50 (H^+ form, 80 to 100 mesh). Wash the column with 0·5N-HCl (100 ml) and elute with 5N-HCl (220 ml). Evaporate the eluate under reduced pressure and dissolve the residue in 0·1N-HCl (5 ml), add activated carbon and filter. To an aliquot (0·5 to 4 ml) add M-$NaHSO_3$ (0·5 ml), set aside for 5 min. and add M-tri(hydroxymethyl)-methylamine (4 ml), M-HNO_2 (3·4 ml) and M-KNO_3 (0·3 ml) to give a pH of 7·4 ± 0·05. Dilute to 30 ml and titrate amperometrically with 2 × 10^{-3}N-$AgNO_3$, adding 0·1 ml at intervals of 30 sec. Column recoveries average 88%. The method is applicable to urine, and to blood or extracts of liver, kidney or brain deproteinised with trichloroacetic acid. Only free cystamine is determined. E. C. APLING

4302. **Simplified and specific method for the estimation of choline.** C. J. Ackerman and W. D. Salmon (Dept. of Animal Husbandry and Nutrition, Auburn Univ., Ala., U.S.A.). *Anal. Biochem.* 1960, **1** (4–5), 327–336.—To determine choline in tissues without preliminary extraction, hydrolyse the sample (≃ 2 g) at 95° for 5·5 hr. with 25% (v/v) HNO_3. Add 10N-NaOH to bring the pH above 12, and then 5% ammonium reineckate in methanol. Set the mixture aside in the dark at 5° for 3 hr., then filter, wash the ppt. with n-propanol, shielding it from light, and dissolve it in acetone. Measure the extinction at 526 mμ. This procedure is claimed to be more specific than other reineckate methods. F. POWELL

4303. **Sensitive analytical method for choline.** C. J. Ackerman and M. Chou (Virginia Polytech. Inst., Blacksburg, Va., U.S.A.). *Anal. Biochem.*, 1960, **1** (4–5), 337–343.—The micro-method described is based on the u.v. absorption of choline reineckate. *Procedure*—Hydrolyse the homogenised tissues with 15% HNO_3 for 2·5 to 4·5 hr. at 100°. Add the calculated amount of 2N-NaOH to adjust the hydrolysate to be 0·1 to 0·2N in NaOH, then filter through sintered glass. Add 5% methanolic ammonium reineckate to the filtrate, chill for 4 hr., then centrifuge and wash the ppt. with n-propanol. Dry the ppt. in the dark over H_2SO_4, then dissolve it in acetone and to a 0·1-ml aliquot add 5 ml of conc. aq. NH_3 and make up to 10 ml with H_2O. Measure the extinction at 303 mμ. Beer's law is obeyed in the range 1 to 16 μg of choline per ml. F. POWELL

4304. **New reagent for the assay of indole in the tryptophanase reaction.** J. M. Turner (Dept. of Biochem., Univ. of Leeds, England). *Biochem. J.*, 1961, **78** (4), 790–792.—*p*-Dimethylaminocinnamaldehyde is used, instead of the usual Ehrlich reagent, in a colorimetric method for the determination of indole. The sensitivity of the method under specified conditions is more than 2·2 times that when *p*-dimethylaminobenzaldehyde is used. The extinction is measured spectrophotometrically at 640 mμ, 30 min. after development of the colour. Amounts of indole of ≮ 1 μg in 20 ml of aq. soln. can be determined by this modified method. J. N. ASHLEY

4305. **Determination of haptoglobins in normal human serum.** H. Smith and J. A. Owen (Clin. Biochem. Lab., St. Vincent's Hosp., Melbourne, Australia). *Biochem. J.*, 1961, **78** (4), 723–728.—Under certain conditions the combination of haptoglobin with haemoglobin or methaemoglobin increases the peroxidase activities of the two proteins. This is the basis of the determination in which the guaiacol - H_2O_2 reaction is used. The dil. serum is mixed with a soln. of methaemoglobin. After being kept for 10 min. this soln. is added to the guaiacol reagent at 25°, and aq. H_2O_2, pre-warmed to 25°, is added immediately. After 10 min. the extinction is determined spectrophotometrically at 470 mμ and the amount of haptoglobin is ascertained from a standard graph. J. N. ASHLEY

4306. **Protein chromatography on a calcium phosphate gel.** E. S. Zueva, L. S. Markosyan and N. I. Proskuryakov (Inst. of Biochem., Acad. Sci. USSR, Moscow). *Biokhimiya*, 1961, **26** (2), 209–211.—The protein sample (50 mg) is dissolved in 2 ml of 0·005M-phosphate buffer (pH 6·8) and applied to a column (1·5 cm × 15 cm) of hydroxyapatite gel (*cf.* Tiselius *et al.*, *Anal. Abstr.*, 1957, **4**, 3502). The column is eluted successively with 45-ml portions of 0·025M-, 0·05M- and 0·1M-buffer of the same pH value, at a rate of 3 ml in 20 to 40 min. The protein is determined spectrophotometrically in each fraction. A. BURWOOD-SMITH

4307. **Production of electrophoretically homogeneous fractions of serum proteins by a salt partition method.** A. S. Volynskii and K. Kh. Khadzhiev (State Med. Inst., Tashkent). *Biokhimiya*, 1961, **26** (2), 217–220.—A simple method is proposed for the successive isolation of electrophoretically homogeneous γ-globulins of anti-diphtheria serum. *Procedure*—The serum (100 ml) is diluted with 400 ml of phosphate buffer (0·1M-KH_2PO_4 and 0·2M-$Na_2B_4O_7$) (pH 6·8). The soln. is heated on a water bath to 37° to 40° and a first fraction is pptd. with 12 to 14 g of Na_2SO_4 and separated by centrifuging at 8000 r.p.m. for 5 to 6 min. Further fractions are pptd. by adjusting the concn. of Na_2SO_4 to 14 to 16, 16 to 18, 18 to 20 and 20 to 22 g per 100 ml successively. The fractions are purified by repeated pptn. or by treatment with $Al(OH)_3$ at a strictly controlled pH. Repptn. of the first fraction is carried out at pH 7·6, the second at pH 5·8, the third and fourth at pH 6·4, and the fifth at 7·8. A. BURWOOD-SMITH

4308. **New technique for direct detection of glycoproteins and polysaccharides after electrophoresis or immunoelectrophoresis in agar gel.** J. Uriel and P. Grabar (Service de Chim. Microbienne, Inst. Pasteur, Paris, France). *Anal. Biochem.*, 1961, **2** (1), 80–82.—The method is based on the formation of the aryl hydrazones of

glycoproteins and polysaccharides after oxidation with periodic acid. Subsequently the hydrazones are converted into copper complexes of formazan derivatives by coupling with a diazonium salt, followed by treatment with Cu acetate. The zones or specific precipitation lines are coloured a stable blue - violet. E. C. BUTTERWORTH

4309. **Identification of nucleic acid components by a combined method of electrodialysis and circular paper chromatography.** E. K. Alimova, G. D. Bolgova and A. T. Astvatsatur'yan (State Med. Inst., Rostov-on-Don). *Biokhimiya*, 1961, **26**(2), 221–224.—A sample (10 mg) of nucleic acids is hydrolysed with N-H_2SO_4 (0·5 ml) on a water bath for 1 hr., then neutralised with $Ba(OH)_2$. The $BaSO_4$ formed is separated by centrifuging, and the supernatant liquid is diluted to 10 ml for electrodialysis at 100 V and 20 mA for 25 to 30 min. The resulting cathode fraction contains the purine bases, the neutral one carbohydrates and the anode one pyrimidine nucleotides. The anode fraction is re-hydrolysed with $HClO_4$ and electrodialysed to liberate free pyrimidine bases. The partition and identification of the compounds of each fraction are carried out by paper chromatography. The cathode fraction is evaporated to dryness, and the residue is dissolved in 0·2 ml of H_2O. Portions (0·01, 0·005, 0·002 and 0·001 ml) of this soln. are placed at a distance of 1 cm from the centre of a circular filter-paper in alternate segments. Control soln. of guanine, adenine, thymine and uracil are used in the other segments. The chromatogram is developed with n-butanol - 0·1N-aq. NH_3 (7 : 1) for 3 hr. The procedure is similar for the anode fraction. The neutral fraction is evaporated to dryness and the residue is dissolved in 0·4 ml of H_2O. Chromatography is carried out in n-butanol - acetic acid - H_2O (4 : 1 : 5) and control soln. of ribose, arabinose, glucose and a mixture of all three are used.
A. BURWOOD-SMITH

4310. **Rapid quantitative determination of total and free cholesterol with anthrone reagent.** G. V. Vahouny, C. R. Borja, R. M. Mayer and C. R. Treadwell (Dept. of Biochem., George Washington Univ. School of Med., Washington, D.C.). *Anal. Biochem.*, 1960, **1** (4–5), 371–381.—A simple, rapid, colorimetric micro-determination of free and total 3β-hydroxysteroids (mainly cholesterol) in serum, lymph and tissues is described. After extraction and saponification of the esterified sterols by established procedures, the total sterol is pptd. in 15 min. at 45° as the digitonide in the presence of dil. HCl and 10% $AlCl_3$ soln. The sterol digitonide is recrystallised twice from methanol - 10% $AlCl_3$ soln. (1 : 1), washed with acetone and suspended in acetic acid, and the digitonin is determined by means of an anthrone reagent stabilised with thiourea. The final colour, measured at 600 mμ, is stable for 24 hr. in the dark. The free sterol is determined similarly, but the saponification stage is omitted. The accuracy is comparable with that of Liebermann - Burchard procedures, but the sensitivity and precision are greater. Less than 20 μg can be determined accurately.
F. POWELL

4311. **Thin-layer chromatography of fats. II. Separation of cholesteryl fatty-acid esters.** H. P. Kaufmann, Z. Makus and F. Deicke (Dtsch. Inst. f. Fettforsch., Münster). *Fette, Seif., Anstrichmitt.*, 1961, **63** (3), 235–238.—Pure cholesteryl esters of 15 saturated and unsaturated fatty acids were prepared and studied. It was found that esters of short-chain and unsaturated fatty acids can be separated on unimpregnated silica-gel plates (Kieselgel G). A two-dimensional method on plates made hydrophobic with liquid paraffin is described, which can be used for the separation of a mixture of these esters with the esters of long-chain fatty acids. Results for various mixtures are given.
I. DICKINSON

4312. **Separation of steroids by gas chromatography.** W. J. A. Vanden Heuvel, C. C. Sweeley and E. C. Horning (Lab. of Chem. of Natural Products, Nat. Heart Inst., Bethesda, Md., U.S.A.). *J. Amer. Chem. Soc.*, 1960, **82** (13), 3481–3482.—Steroid hydrocarbons, ketones, alcohols, ethers and esters can be separated in 2 to 80 min. on a column (180 cm × 0·4 cm) containing 2 or 3% of the methyl-substituted silicone gum SE-30 on Chromosorb W (in 80 to 100-mesh powder) at a temp. of 222°. Relative retention data are listed for 21 compounds. Operation at 260° with 7% of SE-30 appears to cause decomposition of sterols and their acetates. A. R. ROGERS

4313. **Determination of oestrogens as phenols.** A. D. Marenzi and E. S. Braegger (Buenos Aires Univ., Argentina). *Rev. Asoc. Bioquim. Argentina*, 1960, **25**, 73–76.—The sample of oestrogen (20 to 200 μg) in aq. ethanolic soln. is treated with tungstomolybdophosphate reagent (Folin and Ciocalteu), followed by Na_2CO_3 and then Na_2SO_3 soln., and the blue colour is measured photometrically at 720 mμ. Oestrone, oestriol and oestradiol all give similar extinction coefficients, so that an average value (3·38 for 1 mg in 15 ml) can be used with an error of $< 5\%$.
L. A. O'NEILL

4314. **Study of the colorimetric estimation of 17β-oestradiol, 17α-oestradiol, oestrone, oestriol and 16-epioestriol by the Kober reaction.** W. Nocke (Chem. Abt., Chirurg. Univ. und Poliklinik, Bonn-Venusberg, Germany). *Biochem. J.*, 1961, **78** (3), 593–602.—Optimum conditions for the determination are studied. The best conditions for the formation of the yellow colour are almost identical with those described by Brown (*Anal. Abstr.*, 1955, **2**, 3161), but those for the conversion of the yellow into the pink colour differ markedly. This conversion is favoured by (*i*) decreased concn. of H_2SO_4, (*ii*) increased time of heating, (*iii*) presence of oxidising agents, and (*iv*) u.v. light. Excess of any of these factors causes fading of the final pink colour. The important point for complete conversion of yellow into pink is the final concn. of H_2SO_4 in the second stage of the reaction. The pink colour formed under optimum conditions is stable for at least 24 hr. in the absence of bright light. Urinary contaminants decrease the intensity of the colour given by phenolic steroids, but the effects are small and reproducible when the colour reaction is used in connection with the method of purification described by Brown. 17α-oestradiol behaves very differently from its 17β-epimer and other oestrogens. The first stage of the reaction occurs within a few minutes at room temp. and an intense Kober colour is readily obtained, which is very susceptible to changes in the reaction conditions. J. N. ASHLEY

4315. **Fluorimetric determination of adrenocortical steroids.** H. Braunsberg and V. H. T. James (Dept. Chem. Path., St. Mary's Hospital

Med. Sch., London, England). *Anal. Biochem.*, 1960, **1** (6), 452–468.—The determination of corticosterone, hydrocortisone, cortisone and 11β-hydroxyandrostenedione by measurement of their fluorescence in H_2SO_4 has been studied with reference to the sensitivity and precision of the method. R. A. BRENAN

4316. **Simple method for the determination of urinary adrenocortical steroids (α-ketols).** G. R. Kingsley and G. Getchell (Clin. Biochem. Lab., Veterans Admin. Center, Los Angeles, Calif., U.S.A.). *Anal. Biochem.*, 1961, **2** (1), 1–14.—A modification of the blue tetrazolium ketol methods of Chen *et al.* (*Anal. Abstr.*, 1954, **1**, 1019), Recknagel and Litteria (*Ibid.*, 1957, **4**, 1948) and Izzo *et al.* (*J. Clin. Endocrin. & Metabolism*, 1957, **17**, 889) is described. *Procedure*—Hydrolyse urine (7 ml) in a glass stoppered tube with conc. HCl (1 ml) in a boiling-water bath for 3 to 4 min. and extract the cooled hydrolysate with $CHCl_3$ (7 ml) by shaking vigorously for 1 min. Centrifuge, remove the urine layer and wash the extract successively with 10% NaOH soln. (1 ml) and water (3 × 5 ml). Evaporate duplicate 1-ml portions of the extract to dryness on a water bath at 80°. Treat a reagent blank (7 ml of saline) and cortisone acetate standards (0·04 to 0·2 mg in 1 ml of ethanol added to 7 ml of saline) in the same manner. Dissolve the dried residues in 2 ml of ethanol, and add 2 ml of blue tetrazolium reagent (100 mg of blue tetrazolium in 400 ml of ethanol) and 1 ml of 0·03N-ethanolic NaOH. Mix and allow to stand for 15 min., then add 0·2 ml of 3·6% ethanolic HCl, mix thoroughly and read at 525 mμ against the blank soln. For the urine blank, substitute 2 ml of ethanol for the blue tetrazolium reagent. Good recoveries of cortisone or cortisone acetate added to urine are obtained. The addition of glucose (up to 5%) or of androst-5-en-17-one, androsterone, oestrone, progesterone, pregnanediol or pregnanetriol does not cause interference. E. C. BUTTERWORTH

4317. **Absorption spectra of Δ^5-3β-hydroxysteroids in several sulphuric acid reagents.** H. Wilson (Nat. Inst. of Arthritis and Metabolic Diseases, Bethesda, Md., U.S.A.). *Anal. Biochem.*, 1960, **1** (4–5), 402–416.—The absorption spectra between 200 and 700 mμ of 11 Δ^5-3β-hydroxysteroids were determined at room temp. in (*i*) H_2SO_4 - ethanol (4:1), (*ii*) H_2SO_4 - ethanol (2:1) and (*iii*) conc. H_2SO_4. All but three spectra, which had other characteristic peaks, gave typical high peaks near 408 mμ in the ethanolic reagents. Pregn-5-ene-3β,17α,20α-triol showed an unusual range of colours in reagent (*i*), turning deep blue-violet in 30 to 40 min. The ethanolic reagents provide means for simultaneous identification and determination of these steroids. Distinctive curves were also given by a number of other steroids. The reagents are useful for locating compounds on paper chromatograms and in column eluates. There is little to choose between the ethanolic reagents, which are generally more sensitive than H_2SO_4 alone. The absorption curves change with time and the changes can be used as an aid to identification. F. POWELL

4318. **Rapid method for the quantitative assay of proteolytic enzymes.** W. L. Nelson, E. I. Ciaccio and G. P. Hess (Dept. of Biochem., Cornell Univ., Ithaca, New York). *Anal. Biochem.*, 1961, **2** (1), 39–44.—In the determination of pepsin and trypsin, the substrates used (prep. given) are, respectively, indigo carmine - fibrin and Congo red - hide powder, and the soluble products of hydrolysis are measured spectrophotometrically. *Procedure*—For pepsin, the enzyme soln. is adjusted to a pH of 1·7 to 1·8 with HCl, and for trypsin the reaction is carried out in 0·1M-phosphate buffer at pH 7·5. The substrate (100 to 150 mg) is incubated at 35° for 30 min. with 0·5 ml of enzyme soln.; a blank tube contains 0·5 ml of 0·018M-HCl or 0·1M-phosphate. The contents of the tubes are diluted to 50 ml with acid or buffer, shaken vigorously (10 sec.) and filtered. The coloured filtrates are measured at 620 mμ and 495 mμ, respectively, for indigo carmine - fibrin and Congo red - hide powder substrates. Standard curves are constructed from salt-free pepsin and trypsin that have been recrystallised 3 times. E. C. BUTTERWORTH

4319. **Determination of lactic dehydrogenase with a tetrazolium salt.** M. M. Nachlas, S. I. Margulies, J. D. Goldberg and A. M. Seligman (Sinai Hospital, Baltimore, Md., U.S.A.). *Anal. Biochem.*, 1960, **1** (4–5), 317–326.—A sensitive and simple colorimetric method for measuring lactic dehydrogenase activity is described. 2-*p*-Iodophenyl-3-*p*-nitrophenyltetrazolium chloride is used as hydrogen acceptor and phenazine methosulphate as intermediate electron carrier. Gelatin is employed to keep the formazan in colloidal suspension and also improves the electron transfer. The importance of avoiding haemolysis in serum determinations is stressed. F. POWELL

4320. **Determination of human-serum-cholinesterase activity with o-nitrophenyl butyrate.** A. R. Main, K. E. Miles and P. E. Braid (Occupational Hlth Div., Dept. of Nat. Hlth and Welfare, 45 Spencer St., Ottawa, Canada). *Biochem. J.*, 1961, **78** (4), 769–776.—The rapid, sensitive, colorimetric method described is suitable for routine analysis. The cholinesterase liberates *o*-nitrophenol from *o*-nitrophenyl butyrate under easily reproduced and relatively non-critical conditions. The *o*-nitrophenol is determined, in the reaction medium, spectrophotometrically at 414 mμ and pH 7·6. The accuracy of the method is $\pm$ 2·5%, and only 0·004 ml of serum is needed for each determination. J. N. ASHLEY

4321. **Rapid spectrophotometric assays for snake-venom L-amino-acid oxidase based on the oxidation of L-kynurenine or 3,4-dehydro-L-proline [3-pyrroline-2-carboxylic acid].** H. Weissbach, A. V. Robertson, B. Witkop and S. Udenfriend (Nat. Heart Inst., Bethesda, Md., U.S.A.). *Anal. Biochem.*, 1960, **1** (4–5), 286–290.—L-Amino-acid oxidase can be assayed by incubating 0·5 μmole of L-kynurenine, 100 μmoles of tri(hydroxymethyl)-methylamine buffer (pH 8·0), enzyme and water, in a total vol. of 1 ml, and following the increase in extinction at 331 mμ. It can also be assayed by incubating 30 μmoles of 3,4-dehydro-L-proline, 50 μmoles of buffer, enzyme and water, in a total vol. of 1 ml, and measuring the increase in extinction at 261 mμ. Both methods are rapid, simple and sensitive. F. POWELL

4322. **Determination of histaminase in blood by production of ammonia.** A. D. Marenzi, B. M. Lozzio and M. Royer (Buenos Aires Univ., Argentina). *Rev. Asoc. Bioquim. Argentina*, 1960, **25**, 77–83.—The histaminase in blood is determined

from the ammonia produced by enzymatic decomposition of histamine. The sample of blood serum is treated with histamine soln. at pH 7·2 and incubated at 37° for 24 hr. The soln. is then deproteinised and the NH_3 is determined photometrically after addition of Nessler reagent. A blank determination is carried out in which the histamine is added after the incubation. Complete recovery of pig's kidney histaminase added to blood serum was obtained. L. A. O'NEILL

4323. **Determination of small quantities of coenzyme Q and related compounds in biological materials.** J. Jayaraman and T. Ramasarma (Dept. of Biochem., Indian Inst. of Science, Bangalore). *J. Sci. Ind. Res., India, C*, 1961, **20** (3), 69–77.—Conventional methods for isolating and determining coenzyme Q (**I**) and related substances in biological materials are described and compared with respect to their suitability for given materials. Saponification is necessary for materials with a high lipid content, but cannot be used when determining vitamin K. Ubichromenol and **I** are determined by the Emmerie - Engel reaction after chromatographic separation. Vitamin K_1 and menadione are determined colorimetrically. The paper-chromatographic separation of vitamin K_1 and **I** is studied, and degradation products produced by reaction on the column are characterised with respect to their spectral and chromatographic behaviour. A method for determining small quantities of **I** and ubichromenol by means of reverse-phase chromatography is given. R. PRESSER

See also Abstracts—**4062**, ^2H in urine. **4124**, PO_4^{3-} in the presence of labile phosphorus compounds. **4147**, Determination of S^{2-}. **4210**, Titration of -SH groups. **4219**, Sugars by thin-film chromatography. **4334**, Oestradiol dipropionate in oils. **4345**, Hg and Ag in biol. materials. **4348**, Maltotriose in starch conversion products. **4349**, Free amino-acids in flour and bread. **4439**, Liquid scintillator for ^{14}C and ^3H.

Pharmaceutical analysis

4324. **Ion exchange in pharmaceutical analysis.** J. A. P. Stroes (Pharm. Lab., Rijksuniv., Groningen, Netherlands). *Pharm. Weekbl.*, 1961, **96** (5), 165–178 (in English).—The separation of seven combinations of drugs by ion exchange and subsequent determinations in the eluates, mainly by u.v. spectrophotometry, are described. The following compounds are included—acetylcarbromal, isopropylphenazone, caffeine, phenacetin, papaverine hydrochloride, acetylsalicylic acid, colloidal $Al(OH)_3$, neobenodine (*p*-methyldiphenhydramine) maleate, ascorbic acid, caffeine citrate, ephedrine hydrochloride, allylisobutylbarbituric acid, phenazone, theophylline, amidopyrine, butobarbitone and isoprenaline sulphate. M. J. MAURICE

4325. **Assay of certain alkaloids in non-aqueous solution.** S. M. Wang and R. W. Hunter (Southern Coll. of Pharm., Mercer Univ., Atlanta, Ga., U.S.A.). *J. Pharm. Sci.*, 1961, **50** (3), 265.—Prepare a soln. of the sample (containing 5 to 50 mg of alkaloid) in H_2O or dil. acetic acid (25 ml) and slowly add 1% mercuric acetate soln. (10 ml). Shake the mixture for 30 min. with Amberlite IRC-50 (H^+ form) (1 g), filter and allow the solid to drain on the filter. Heat the solid with glacial acetic acid (25 ml) at 60° for 10 min., shake for 30 min. and titrate with 0·01N-$HClO_4$ in acetic acid, with methyl violet as indicator. The procedure can be applied to tablets and plant extracts as well as to pure alkaloids and their salts. The coeff. of variation is $\simeq$ 0·25%. A. R. ROGERS

4326. **Nitration of strychnine and its polarographic determination.** G. Dušinský (State Inst. for Control of Drugs, Bratislava, Czechoslovakia). *Českosl. Farm.*, 1961, **10** (4), 181–186.—Polarographic, oscillopolarographic and u.v. spectrophotometric methods were used for studying the products and the velocity of the nitration of strychnine in 3·1M to 6·9M-HNO_3 (alone and in admixture with $HClO_4$) at normal and elevated temp. The velocity constants correspond to the formation of dinitrostrychnine, which is polarographically reducible, yielding a 10-electron double wave in an alkaline medium; at a pH of 11·5, $E_{\frac{1}{2}} = -0{\cdot}64$ V and $-0{\cdot}79$ V *vs.* the S.C.E. *Procedure*—To a soln. (2 ml, containing 0·01 to 0·5 mg of strychnine) add HNO_3 ($d = 1{\cdot}41$) (1 ml) and heat in a stoppered test-tube in a boiling-water bath for 20 min. Cool, add 2·5M-KOH (8 ml), remove O with a stream of N and record the polarogram from $-0{\cdot}4$ V. Compare with a calibration curve. To accelerate the determination, a mixture of HNO_3 (0·7 ml) with $HClO_4$ (70%) (1 ml) is used and heated for 4 min. at 100° with 1·3 ml of the test soln., and the mixture is made alkaline with 8 ml of 2·5N-NaOH. For samples containing $< 0{\cdot}01$ mg of strychnine, the test soln. is evaporated to dryness, H_2O (0·2 ml) and conc. HNO_3 (0·1 ml) are added and the nitration and polarography are carried out as described above, with one-tenth of the vol. of the reagents. As little as 1 μg can be determined. Strychnine can be determined in admixture with brucine (10:1 or 1:10) after a previous separation of brucine by paper chromatography (Dušinský and Tyllová, *Anal. Abstr.*, 1959, **3**, 697). The procedures described were tested on strychnine injections and extracts of nux vomica. J. ZÝKA

4327. **Ion-exchange method for the determination of strychnine in nux vomica and its preparations.** W. Kamp and C. P. C. Post (Pharm. Lab., Rijksuniv., Utrecht, Netherlands). *Pharm. Weekbl.*, 1961, **96** (5), 179–184.—The total alkaloids are isolated with the cation-exchange resin Dowex 50-X2 by the method of Kamp (*Anal. Abstr.*, 1957, **4**, 1954). Strychnine and brucine in 2N-HCl are separated by means of the anion-exchange resin Dowex 1-X2, $[Fe(CN)_6]^{4-}$ form, that has previously been washed with 2N-HCl. After $\lesssim$ 12 hr. brucine is eluted with N-HCl. Strychnine is then eluted with N-ethanolic NH_3. After extraction with $CHCl_3$, strychnine is determined volumetrically. The completeness of the separation was demonstrated by paper chromatography of the separated and isolated alkaloids. M. J. MAURICE

4328. **Comparative study of the different photometric methods of determination of atropine. I.** I. R. Fahmy, Z. F. Ahmed and S. A. Eid (Nat. Res. Centre Dokki, Cairo). *J. Chem. U.A.R.*, 1961, **3** (2), 229–240.—The tungstosilicic acid, tungstophosphoric acid, copper sulphate, sodium picrate and *p*-dimethylaminobenzaldehyde methods are unsuitable for the micro-determination of atropine in toxicological samples. Vitali's method is preferred. *Procedure*—Add aq. NH_3 to an aq. soln. of the sample (containing 10 to 150 μg of atropine) until alkaline and extract with $CHCl_3$

(3 × 10 ml). Evaporate the combined extracts, add fuming HNO_3 ($d = 1{\cdot}50$) (10 drops) and evaporate again. Dissolve the residue in a mixture of anhyd. ethanol and acetone (3:97) (10 ml), add 6% methanolic KOH (5 drops) and measure the extinction at 575 mμ after exactly 2 min. Tropine does not interfere.

II. I. R. Fahmy, Z. F. Ahmed and S. A. Eid. *Ibid.*, 1961, **3** (2), 241–250.—The use of bromothymol blue, bromocresol purple, Metanil yellow (C.I. Acid Yellow 36) and methyl orange, and various organic solvents, in the alkaloid - dye method of determination has been studied. The combination of Metanil yellow and $CHCl_3$ is most convenient. *Procedure*—Mix 0·2% Metanil yellow soln. (50 ml) with McIlvaine Na_2HPO_4 - citric acid buffer soln. (pH 7) (50 ml) and shake with $CHCl_3$ until no more dye is extracted. To the aq. soln. of the sample (containing 20 to 150 μg of atropine) add dye - buffer soln. (2 ml), dilute to 15 ml with H_2O and extract with $CHCl_3$ (3 × 10 ml). Shake the combined extracts with 0·1N-HCl (2 × 10 ml), combine the aq. phases and measure their extinction at 540 mμ against a reagent blank. Tropine interferes.

A. R. Rogers

4329. **Some aspects of the polarographic determination of atropine and hyoscyamine.** T. J. Benraad and O. F. Uffelie (Pharm. Lab., Rijksuniv., Utrecht, Netherlands). *Pharm. Weekbl.*, 1961, **96** (6), 201–219.—Experimental evidence is produced which indicates that the reaction of atropine at the dropping mercury electrode in 0·1N-LiCl is a simple reduction process. The abnormal behaviour of the current - voltage curve shown by atropine soln. in a borate buffer at varying temp., concn. and height of the mercury column may be explained by assuming that the reduced atropine forms a complex with borate anion, which catalyses the hydrogen-ion reduction. M. J. Maurice

4330. **Analysis of the alkaloid content of ergot.** T. G. Alexander and D. Banes (Div. Pharm. Chem., Food and Drug Admin., Washington, D.C., U.S.A.). *J. Pharm. Sci.*, 1961, **50** (3), 201–204.—Extract the powdered ergot (5 g) with aq. NH_3 - methanol - $CHCl_3$ (1:9:90) and determine the total alkaloids in an aliquot colorimetrically with *p*-dimethylaminobenzaldehyde reagent. Transfer another aliquot to a chromatographic column of Celite 545, remove the water-insoluble alkaloids by washing with $CHCl_3$, then elute with 0·2N-H_2SO_4 and determine the water-soluble alkaloids colorimetrically in the eluate. Use a 0·1M-citric acid trap at the bottom of the column to ensure retention of ergometrine and ergometrinine while ergotamine and ergotoxine are washed out with $CHCl_3$. To determine the relative concn. of ergometrine and ergometrinine, separate chromatographically on paper with the non-aqueous layer of a mixture of n-butyl acetate, nitromethane, 2-ethoxyethyl acetate, pyridine and H_2O (50:25:25:4:5) as mobile phase and phosphate buffer (pH 6) as stationary phase, and examine the fluorescence intensity under u.v. light. The procedure gives higher values for water-soluble alkaloids than does that of the U.S. N. F. X.

A. R. Rogers

4331. **Isolation and detection of aconitine in toxicological analysis.** S. Narain Tewari (18/3A The Mall, Kanpur, India). *Z. anal. Chem.*, 1961, **180** (1), 36–37 (in English).—For isolation, macerate the tissue (50 to 100 g) with 5% acetic acid (350 ml) and saturate the slurry with $(NH_4)_2SO_4$. Heat on a water bath for 30 min. and filter through paper pulp. Wash the ppt. with 5% acetic acid (2 × 250 ml). Extract the combined filtrates with an equal vol. of ether. Make the aqueous phase alkaline with aq. NH_3 and re-saturate with $(NH_4)_2SO_4$. Extract twice with ether (equal vol.) and evaporate the ether to obtain the alkaloid. Aconitine is detected by its action on the tongue or by its toxic action on frogs. Further identification is given by paper chromatography on Whatman No. 1 paper buffered with 5% sodium dihydrogen citrate soln. The solvent system is n-butanol - water - citric acid (Curry and Powell, *Anal. Abstr.*, 1954, **1**, 2508). Detection is by u.v. fluorescence or K_2PtCl_4 soln. The R_F of aconitine is 0·84 and the detection limit 5 μg. A microcrystalline test is also described. The u.v. absorption max. of aconitine in 0·1N-H_2SO_4 is at 235 mμ.

G. Russell

4332. **Polarographic determination of tubocurarine in pharmaceutical specialities.** G. Alessandro and F. Dal Brollo (Farmitalia, Milan, Italy). *Farmaco, Ed. Prat.*, 1961, **16** (3), 138–143.—Prepare a soln. containing tubocurarine chloride (**I**) (30 to 70 mg) in H_2O (100 ml). To this soln. (2 ml) add fuming HNO_3 ($d = 1{\cdot}4$) (0·1 ml) and boil for exactly 1 min. Cool, add N-NaOH till the colour changes to pink - violet, dilute to 10 ml with McIlvaine citrate - phosphate buffer (pH 7) and examine polarographically after de-aerating with N for 5 min. For concn. of **I** from 0·2 to 0·8 mg per ml the error of the current to concn. ratio is ≯ 3%; the $E_{\frac{1}{2}} = 0{\cdot}43$ V. The method is applicable to soln. for injection (0·3%), 2 ml of a 1:10 dilution being taken. For suppositories (containing 4·5 mg of **I**), 5 are dissolved in $CHCl_3$ (30 ml) and extracted several times with 0·1N-H_2SO_4 to a total of 50 ml; an aliquot (2 ml) of the H_2SO_4 soln. is treated as described above. Oxidised **I** shows no polarographic wave and does not interfere.

J. I. M. Jones

4333. **Separation of tetracycline antibiotics on a cellulose column.** O. Hrdý and P. Veselý (State Inst. for Control of Drugs, Prague). *Českosl. Farm.*, 1961, **10** (3), 126–130.—A column of powdered cellulose, impregnated with ethyl acetate saturated with 0·5M-tartrate buffer soln. of pH 3, is used. The samples are dissolved in tartrate soln. (2 to 4 mg per ml) and ≯ 0·25 ml is placed on the column. The column is then washed with ethyl acetate saturated with tartrate buffer soln. and the separated fractions are detected in u.v. light (mercury lamp). Chlortetracycline, tetracycline, oxytetracycline, epichlortetracycline and epitetracycline produce a red fluorescence and anhydrochlortetracycline and anhydrotetracycline an intense yellow one. The fractions are evaporated and the antibiotics assayed in the usual way.

J. Zýka

4334. **Determination of oestradiol dipropionate in oils.** D. W. Snair and L. A. Schwinghamer (Food & Drug Lab., Dept. of Nat. Health and Welfare, Ottawa, Canada). *J. Pharm. Pharmacol.*, 1961, **13** (3), 148–153.—Variable results are obtained in the determination of oestradiol dipropionate in pharmaceutical preparations by the method of the U.S.P. XVI. Oestradiol (**I**) can be determined absorptiometrically after hydrolysis in acid soln., but interfering substances present in the solvent oil must first be removed chromatographically. *Procedure*—Dilute the sample (1 or 2 ml containing 1 mg of steroid) with n-hexane (5 ml) and

apply to a chromatographic column of Celite 545 (5 g) which has been wetted with iso-octane (25 ml) and polyoxyethylene glycol 600 (2 ml). Elute with n-hexane and collect 75 ml. Evaporate to dryness in a stream of air, add methanol (10 ml) and conc. HCl (0·5 ml) and heat under reflux for 15 min. Evaporate in a stream of air, dilute with light petroleum (boiling-range 30° to 50°) (60 ml) and extract with N-NaOH (5 × 10 ml). Bring the combined extracts to pH 2 to 3 with 10N-H_2SO_4, set aside for 1 hr. and extract with $CHCl_3$ (4 × 15 ml). Evaporate the $CHCl_3$ extracts to dryness, dissolve the residue in ethanol and determine **I** by the method of the U.S.P. XIV with iron - phenol reagent. A. R. ROGERS

4335. **Estimation of folic acid in multivitamin - mineral preparations.** O. Pelletier and J. A. Campbell (Food and Drug Lab., Dept. of Nat. Health and Welfare, Ottawa, Ont., Canada). *J. Pharm. Sci.*, 1961, **50** (3), 208–212.—The use of a standard blank extinction reading improves the accuracy of the method of Schiaffino *et al.* (*J. Amer. Pharm. Ass., Sci. Ed.*, 1959, **48**, 236). Interference caused by $FeSO_4$ is eliminated by addition of ascorbic acid and that of ferric ammonium citrate by chelation with EDTA. Red dyes in certain preparations and pigments in some biological extracts cannot be removed completely by extraction with isobutyl alcohol, but can be allowed for by use of the appropriate blank readings. Low recovery of folic acid in the presence of some multivitamin - mineral mixtures is overcome by the use of a soln. containing Na_3PO_4 and Ca lactate as an extraction medium instead of K_2HPO_4 soln.; with this mixed extractant, ferrous gluconate causes interference, but this is eliminated by the use of EDTA. *p*-Aminobenzoic acid interferes, but can be extracted quantitatively with a 5% soln. of benzoic acid in ethyl acetate. A. R. ROGERS

4336. **Extraction and identification of barbiturates.** M. T. Bush (Dept. Pharmacol., School of Med., Vanderbilt Univ., Nashville, Tenn., U.S.A.). *Microchem. J.*, 1961, **5** (1), 73–90.—The theoretical and practical aspects of solvent extraction as a general method for the recovery, purification and identification of drugs and their metabolic products are discussed, with special reference to the barbiturates. Values are given of partition coeff. of a few representative barbiturates between water and (*i*) ethyl ether, (*ii*) isopropyl ether, (*iii*) dichloromethane and (*iv*) n-butyl chloride at 24° to 26°, and these show that solvents (*i*), (*iii*) and (*iv*) are all satisfactory for the removal of the most common barbiturates from aq. soln. at pH 6. Criteria as to the nature and purity of the extracted 'barbiturate' may be obtained by recording the absorption spectrum of an aq. extract from the solvent at pH 10·5 over the range 400 to 220 mμ. Further evidence as to the identity of the substance can be obtained by a study of second ionisation constants, R_F values and, if necessary, infra-red spectra. I. A. SIMPSON

4337. **Use of mixed indicators in the control of drugs. III. Determination of soluble barbitone and phenobarbitone.** M. Zahradníček, V. Benediktová and E. Michalcová (Pharm. Fac., Univ. Brno, Czechoslovakia). *Českosl. Farm.*, 1961, **10** (3), 130–133.—*Procedure for barbitone*—Dissolve the sample (0·4 g), dried for 3 hr. at 105°, in H_2O (100 ml) and titrate with 0·1N-HCl, with indicator *A* [bromocresol green (0·1% soln. in 95% ethanol) - methyl red (0·1 soln. in 95% ethanol) (6:1)] to a grey end-point. *For phenobarbitone*—Dissolve the sample (0·2 g), dried for 4 hr. at 150°, in H_2O (100 ml) and titrate as described above with indicator *B* [methyl red - bromocresol green (1:8)]. For each titration use 10 drops of the indicator. J. ZÝKA

4338. **Paper electrophoresis of some local anaesthetics.** V. Jokl and V. Sukupová-Kolková (Pharm. Fac., Univ., Bratislava, Czechoslovakia). *Českosl. Farm.*, 1961, **10** (4), 197–199.—The following compounds were studied—cocaine, procaine, amethocaine, benzamine, amylocaine, diperodon, lignocaine, cinchocaine and 3-piperidino-4′-propoxypropiophenone (Falicaine), all as the hydrochlorides. The electrophoresis was carried out on Whatman No. 4 paper, at 20 V per cm, in Britton - Robinson buffer soln. and with 1 μl of the sample (≃ 0·005 to 0·008 mg). Dragendorff's reagent was used for the detection of the separated compounds. J. ZÝKA

4339. **Assay for bithionol in liquid soap.** H. J. van der Pol (N. V. Koninklijke Pharm. Fabrieken v/h, Brocades-Stheeman en Pharmacia, P.O. Box 48, Amsterdam C, Holland). *J. Pharm. Sci.*, 1961, **50** (3), 272.—Although the procedure of Matuszak *et al.* (*cf. Anal. Abstr.*, 1961, **8**, 788) is more accurate than that of van der Pol (*cf. Anal. Abstr.*, 1959, **6**, 2762), the former is restricted to samples of liquid soap, and the soap base (without the bithionol) must be available to the analyst. A. R. ROGERS

4340. **Polarographic and photometric determination of benactyzine hydrochloride.** J. Vachek (Res. Inst. Pharm. and Biochem., Prague). *Českosl. Farm.*, 1961, **10** (4), 187–188.—Benactyzine (**I**) was determined polarographically, or photometrically, after nitration. *Polarographic procedure*—Evaporate the ethanolic soln. of the sample ($2·75 \times 10^{-3}$M), add nitration mixture (HNO_3 - H_2SO_4) (1:1) (0·5 ml), heat for 10 min. in a water bath, cool, add 2N-NaOH (7 ml) and H_2O (2·5 ml), remove O with a stream of N and record the polarogram. *Photometric procedure*—To the evaporated sample add HNO_3 (0·5 ml) and, after 1 min., conc. H_2SO_4 (6·5 ml), mix and after 20 min., measure the extinction against a blank. When determining **I** in pharmaceuticals, the free benzilic acid must be removed by dissolving the sample in 0·5N-HCl and extracting with ether, by the procedure of Jefferies and Phillips (*Anal. Abstr.*, 1957, **4**, 1337). J. ZÝKA

4341. **The use of Reinecke's salt in the analysis of drugs. III. Photometric determination of Diparcol [diethazine], Tofranil [imipramine], Ritalin [methyl phenidate] and azacyclonol.** A. Danek (Dept. of Inorg. and Anal. Chem., Med. Acad., Krakow, Poland). *Dissert. Pharm., Krakow*, 1961, **13** (2), 149–153.—Diethazine, imipramine, methyl phenidate and azacyclonol give crystalline ppt. with Reinecke's salt (**I**). *Procedure*—The test substance (20 to 25 mg) is dissolved in H_2O and acidified with H_2SO_4, and warm satd. **I** soln. is added. The ppt. is filtered off, washed with **I** soln. and H_2O, and dissolved in 50 ml of acetone; then the extinctions at 525 mμ are measured. The results are referred to a standard curve prepared by the same procedure. Beer's law is obeyed in the concn. range 0·2 to 1·0 mg per ml. The error is $\gtrsim \pm 4\%$. B. K.

4342. **Determination of dextrosulphenidol.** A. A. Forist and S. T. Madden (The Upjohn Co., Kalamazoo, Mich., U.S.A.). *J. Pharm. Sci.*, 1961, **50** (3), 269–270.—The method is based on the determination of dichloroacetohydroxamic acid produced by the interaction of dextrosulphenidol with alkaline hydroxylamine. In 8 experiments, the mean recovery was 100·5% and the standard deviation was ± 2·8%. *Procedure*—Mix a soln. of the sample (≃ 9 mg) in anhydrous ethanol (5 ml) with a mixture of a 12·5% soln. of hydroxyammonium chloride in methanol and a 12·5% soln. of NaOH in 85% methanol (1 : 1) (3 ml), heat at 50° for 45 min. in a tightly stoppered flask, dilute to 50 ml with ferric perchlorate reagent, mix, and measure the extinction at 530 mμ against a reagent blank within 1 hr. Simultaneously develop the colour from a standard soln. of dextrosulphenidol. To prepare the ferric perchlorate reagent, mix powdered iron (800 mg) with H_2O (3 ml), slowly add 70% $HClO_4$ (10 ml) and H_2O (7 ml), heat carefully until dissolution is complete, cool and dilute with anhydrous ethanol to 100 ml; mix a 40-ml aliquot with 70% $HClO_4$ soln. (12 ml) and dilute to 1 litre with anhydrous ethanol.

A. R. ROGERS

4343. **Spectrophotometric determination of 2-ethylisonicotinthioamide [ethionamide] in pharmaceuticals.** R. Kraus and Z. Šimáně (Res. Inst. of Tuberculosis, Prague). *Českosl. Farm.*, 1961, **10** (4), 195–197.—Ethionamide (**I**) after treatment with Hofmann reagent yields a brown-red colour suitable for spectrophotometric determination. *Procedure*—To 1 ml of test soln. (≃ 1 mg of **I**) in a 25-ml flask add $NaHCO_3$ soln. (6%), Hofmann reagent [dissolve 0·5 g of $Na_2Fe(CN)_5NO$ in 10 ml of H_2O, add 0·5 g of hydroxyammonium chloride and 1 g of $NaHCO_3$, and, after the evolution of gas has ceased, add 2 drops of bromine, remove the excess with a stream of air, dilute with H_2O to 250 ml, filter and store at 2° to 4° for ≯ 2 weeks] (2·5 ml), dilute to vol. with H_2O and measure the extinction at 475 mμ after 15 min. Procedures for the isolation of **I** from various pharmaceuticals are given.

J. ZÝKA

4344. **Volumetric method for determination of amiphenazole hydrochloride (Daptazole) with sodium tetraphenylborate.** W. Sztark (Dept. of Inorg. and Anal. Chem., Med. Acad., Krakow, Poland). *Dissert. Pharm., Krakow*, 1961, **13** (1), 57–61.—The method is based on the pptn. of amiphenazole hydrochloride (**I**) with Na tetraphenylborate. The ppt. is dissolved in acetone, $HgCl_2$ soln. is added and the liberated HCl is titrated with NaOH. The reactions are—

(*i*) $RNH_2.HCl + Na[B(C_6H_5)_4] = RNH_2.H[B(C_6H_5)_4] + NaCl$

(*ii*) $RNH_2.H[B(C_6H_5)_4] + 4HgCl_2 + 3H_2O = RNH_2.HCl + 4(C_6H_5)HgCl + 3HCl + H_3BO_3$.

Procedure—To the sample soln. (4 mg of **I** in 5 ml of H_2O) add, dropwise, 1% acetic acid, 3% aq. Na tetraphenylborate (0·5 ml) and satd. aq. $NaNO_3$ (1 ml). Filter off the ppt., dissolve it in acetone, add satd. $HgCl_2$ soln. (1 ml), H_2O (10 to 20 ml), methyl red soln. (5 drops) and 0·01N-NaOH (5 ml), and boil. To the boiling soln. add 20% KI soln. (1 ml) and 0·01N-HCl (5 ml), and titrate with 0·01N-NaOH. The method was used for the determination of **I** as the pure substance and in tablets. The standard deviation was 0·072 (20 determinations).

B. K.

4345. **Hydrazine sulphate as a specific reagent for the detection of mercury and silver in toxicological analysis.** H. Romanowski (Dept. of Toxicol. and Forensic Chem., Med. Acad., Lublin, Poland). *Dissert. Pharm., Krakow*, 1961, **13** (2), 155–157.—Hydrazine sulphate can be used for the detection of Ag and Hg in soln. and in biological materials after mineralisation. *Procedure*—To the test soln. (1 ml) add, dropwise, Na K tartrate soln. (to pH 8) and 0·3% aq. hydrazine sulphate (1 ml) and heat for 20 min. at 80° to 90°. The presence of Ag or Hg is indicated by a grey-black ppt. or a turbidity. Silver can be detected in concn. of 1 in 5×10^4 and Hg in concn. of 1 in 3×10^4; Tl, Cu, Bi, Cd, As, Sb, Sn, Cr, Mn, Zn, Ba and Mg do not interfere. A modification for the detection of one metal in the presence of the other is given.

B. K.

See also Abstracts—**4089**, Hg^{II} in presence of organic Hg. **4256**, Polynuclear aromatics in liquid paraffin. **4264**, Analysis of turpentine oil. **4284**, Gold-containing drugs in biol. materials. **4366**, Thin-film chromatography of pyridoxine. **4370**, Chromatographic separation of vitamins A and D. **4386**, Tetracyclines in feeding-stuffs.

Food

Food and food additives, beverages, edible oils and fats, vitamins.

4346. **Examination of the occurrence of honeydew in honey. II.** K. C. Kirkwood, T. J. Mitchell and I. C. Ross (Dept. of Chem. Technol., Royal Coll. of Sci. and Technol., Glasgow, Gt. Britain). *Analyst*, 1961, **86**, 164–165.—Twenty-eight samples of honey were analysed for moisture, ash, colloid, dextrin and reducing sugars, and their specific rotation and pH were measured, the object being to test the efficiency of the discriminant function for distinguishing floral honey from honeydew honey previously reported (Kirkwood *et al.*, *Ibid.*, 1960, **85**, 412) and, in particular, to distinguish Scottish heather honey from honeydew honey. Heather honey was readily identified by its high colloid content and, for samples having the same colloid content, honeydew honeys were much darker. Honeydew honeys had higher dextrin and lower reducing-sugar contents than floral honeys, and all were dextrorotatory, whereas floral honeys were laevorotatory. Ash content and pH values were of no use for discriminating between ling-heather honey and honeydew honey. The efficiency of the discriminant function (*loc. cit.*) was confirmed. Eleven of the 28 samples tested contained honeydew.

A. O. JONES

4347. **Hydroxymethylfurfuraldehyde in honey. I. Determination and conversion of hydroxymethylfurfuraldehyde.** E. Romann and M. Staub (Kanton. Lab., Zürich, Switzerland). *Mitt. Lebensmitt. Hyg., Bern*, 1961, **52** (1), 44–58.—Two methods of determination are described. For 1 to 6 mg of 5-hydroxymethylfurfuraldehyde (**I**) in 100 g of honey, the **I** is extracted by ether from a neutralised, filtered, aq. 5% soln. of sample. The ether is evaporated, the residue is re-dissolved in water, and the extinction is measured at 244, 284 and 324 mμ. For 4 to 40 mg of **I** in 100 g of sample, the extinction is measured at 284 mμ on a similar aq. soln. before and after ether extraction. The method of calculation

is given in both cases. Results presented show a recovery of **I** within $\simeq \pm 10\%$ for the first method and within $\simeq \pm 5\%$ for the second method.

R. CLARKE

4348. **Use of selective desorption from carbon columns for the determination of maltotriose in starch conversion products.** S. J. Patterson and J. L. Buchan (D.S.I.R., Lab. of the Gov. Chemist, Custom House, London, E.C.3). *Analyst*, **1961**, **86**, 160–163.—The method previously described for the determination of glucose and maltose in starch conversion products (Patterson and Savage, *Ibid.*, 1957, **82**, 812) has been extended to the determination of maltotriose. The modifications necessary were the lengthening and narrowing of the column to 15 in. long × 0·5 in. diam., the amount of carbon - kieselguhr mixture being unchanged, and the elution of the column with 100 ml of water for glucose, 100 ml of 5% ethanol for maltose, and 150 ml of 8% ethanol for maltotriose, the temp. being maintained throughout at 40°. To establish the validity of the method, maltotriose was separated from liquid glucose by column chromatography and purified by paper chromatography, and its complete recovery by the method described was effected. It was then used to standardise the Somogyi reagent. Since maltotriose is not available commercially, the figures relating the titre of 0·005N-$Na_2S_2O_3$ to wt. of maltotriose now reported may be used. It is recommended that, unless the determination of maltotriose is required, the shorter column previously described (*loc. cit.*) should be used for determining glucose and maltose. A. O. JONES

4349. **The participation of amino-acids in the reaction of melanoidin formation in bread baking. [Determination of free amino-acids.]** V. L. Kretovich and A. N. Ponomareva (Tech. Inst. of Food Industry, Moscow). *Biokhimiya*, **1961**, **26** (2), 237–243.—The sample of wheat flour, dough or bread, or rye-dough or bread (20 g) is extracted with 140 ml (or, with rye flour, 180 ml) of H_2O at 0°, for 10 min., then the soln. is centrifuged at 2000 r.p.m. for 3 min. The supernatant liquid is diluted with 2 parts by vol. of 95% ethanol (3 parts for rye flour), and left overnight in the cold. The soln. is filtered and evaporated to dryness under vacuum at 45° to 50°. The residue is dissolved in 2 ml of H_2O (10 ml for rye flour) and diluted with 5 parts of 95% ethanol. Amino-acids are separated from sugars and salts on a column (8 cm × 1 cm) of KU–2 resin (H^+ form) that has been washed with 15 to 20 ml of 80% ethanol before use, and the column is washed with 80% ethanol (5 × 20 ml). The amino-acids are eluted with aq. NH_3 (80 ml of 0·4N in 80% ethanol), 30 ml of 80% ethanol, 30 ml of H_2O, 30 ml of 4N-aq. NH_3 and 30 ml of H_2O. The combined eluates are evaporated to dryness under vacuum at 50° to 55°. The residue is dissolved in 2 ml of 10% aq. isopropyl alcohol, and 5 to 30 ml of this soln. is examined and analysed by paper chromatography. A. BURWOOD-SMITH

4350. **The fluoride content of gelatin.** J. C. Bartlet (Food and Drug Lab., Dept. of Nat. Health and Welfare, Ottawa, Ont., Canada). *Analyst*, **1961**, **86**, 200–201.—The sample (5 g) with 25 ml of a N suspension of lime and a few drops of olive oil is dried in a platinum dish and ignited at 600°. The ash is dissolved in $HClO_4$, the F^- are distilled off as H_2SiF_6, and the F^- in an aliquot of the distillate are determined by the thorium - thoron colorimetric procedure (*Brit. Abstr. C*, 1952, 380). Of 82 samples from 10 countries, 59 contained $\geq$ 10 p.p.m. of F^-, 15 contained from 10 to 25 p.p.m. and 8 processed with water containing 1 p.p.m. of added F^- contained 29 to 34 p.p.m. Lime and other chemicals used in the processing may contribute to the F^- content. The minimum level to be expected should probably not exceed 10 p.p.m.

A. O. JONES

4351. **Spectrophotometric determination of fluroral and uranin in milk.** E. A. Corbin (Dairy Products Lab., U.S. Dept. Agric., Washington, D.C., U.S.A.). *J. Dairy Sci.*, 1960, **43** (7), 920–924.—Methods are described for the determination in milk of oil-soluble (fluroral) (**I**) and water-soluble (uranin) (**II**) fluorescein dyes, used as dye-markers in intramammary preparations containing antibiotics. **I** is determined from the extinction at 420 mμ of an ether extract of the sample previously treated with an acidic tungstate reagent to precipitate proteins; 2 μg of **I** per ml of sample can be detected. For the determination of **II**, milk proteins are pptd. with N-NaOH and, after being set aside for 5 min., the mixture is filtered through paper. The filter and residue are washed with N-NaOH to produce a known vol., and the extinction is measured at 480 mμ; 1 μg or more of **II** per ml of sample can be detected.

W. H. C. SHAW

4352. **Detection of hydrogenated fats in butter fat by measurement of *cis-trans* conjugated unsaturation.** J. C. Bartlet and D. G. Chapman (Food and Drug Directorate, Ottawa, Canada). *J. Agric. Food Chem.*, 1961, **9** (1), 50–53.—The practically constant ratio of *cis-trans* conjugated unsaturation to isolated *trans* unsaturation in butter fat, as determined by differential infra-red spectroscopy, was used as a means of detection of hydrogenated fats, which contain only the isolated *trans* unsaturation. A 4·000 ($\pm$ 0·002) % (w/v) soln. of the filtered sample in CCl_4 is examined with the infra-red spectrophotometer and the spectrum is recorded (in duplicate) over the range 1025 to 920 cm^{-1}, with a pure butter (chosen with a middle range of "*trans* acids") in the reference beam. The readings at 967 and 948 cm^{-1} are deducted from the reading at 920 cm^{-1}. To correct these two readings from slight unbalance of the two cells, a reference spectrum is obtained with the reference butter soln. in both beams. For this also the 967- and 948-cm^{-1} readings are deducted from the 920-cm^{-1} reading, and the differences are deducted from the corresponding differences for the sample. The corrected readings thus found are plotted against each other; if the plotted point falls outside the area given by plots for pure butters (enlarged to take in 99% confidence limits), hydrogenated fat is present. C. L. HINTON

4353. **Moisture determination in dates by forced-ventilation infra-red drying.** G. Zimmermann (Div. of Food & Biotechnol., Technion, Israel Inst. of Technol., Haifa). *J. Sci. Food Agric.*, 1961, **12** (3), 240–246.—The disadvantages of methods employing vacuum drying, refractive index, distillation and dielectric measurements are discussed. Results obtained by standard vacuum drying and by toluene distillation are compared and the suitability of the latter as a reference method is established. A method and apparatus for i.r. drying with forced ventilation are described, which

gave reliable and reproducible results. The sample (5 g) is heated with a 250-W lamp for 10 min. at 50 W and then for 15 min. at 60 W, at a pressure of 160 torr and a distance of 30 mm between lamp and sample. I. DICKINSON

4354. **The use and identification of surface-active agents in foodstuffs.** W. Ciusa and G. Barbiroli (Ist. Merceologia, Univ. Bologna, Italy). *Boll. Lab. Chim. Provinciali*, 1961, **12** (1), 30–46.—The tests recommended by the Italian Ministry of Health for the identification of polyoxyethylene esters are examined and shown to lack specificity, giving positive results not only with polyoxyethylene esters but also with other surface-active agents and unknown food constituents. The tests in question are those of Van der Hoeve (*cf.* Brown and Hayes, *Analyst*, 1955, **80**, 755), Muntoni *et al.* (*Rass. Chim.*, 1959, **11**, July–Aug.), Anselmi *et al.* (*Anal. Abstr.*, 1960, **7**, 1578) and Boari (*Anal. Abstr.*, 1960, **7**, 2973). Tables of the reactions of commercial surface-active agents in these tests are given. J. I. M. JONES

4355. **Examination of the purity of food dyes.** L. Piekarski and S. Krauze (Dept. of Bromatology, Med. Acad., Warsaw, Poland). *Roczn. Zakł. Hig., Warsaw*, 1960, **11** (6), 551–555.—A chromatographic method is described for the qual. detection of impurities in 8 dyes. *Procedure*—Apply 10 μl of the test soln. (10 mg of dye per ml of H_2O) to Whatman No. 4 paper (50 cm × 15 cm) and develop the chromatogram with n-butanol - ethanol - H_2O (2:1:1) by the ascending technique for 12 to 24 hr., with pure dyes as comparison standards. B. K.

4356. **Investigations on the spectrophotometric identification of colouring matters for use in foods.** R. De' Gori and F. Grandi (Lab. Chim. Provinciale, Siena, Italy). *Boll. Lab. Chim. Provinciali*, 1961, **12** (1), 60–80.—Tables of the extinctions of neutral, alkaline and acid soln. of synthetic colouring matters permitted in Italy for use in foods are given at 10-mμ intervals from 210 to 600 mμ with graphs showing the ratio of E to $E_{max.}$ over the same range of wavelengths. Aq. soln. (1 mg in 100 ml) were used for all dyes except quinoline yellow (5 mg) and tartrazine (4 mg). The Italian permitted dyestuffs are—Sunset yellow F.C.F. (C.I. Food Yellow 3), quinoline yellow (C.I. Food Yellow 13), tartrazine, indigo carmine, Patent blue V (C.I. Acid Blue 3), Brilliant black BN (C.I. Food Black 1), Azo Rubine (C.I. Acid Red 14), Fast red E (C.I. Food Red 4), Amaranth (C.I. Food Red 9), Ponceau 4R (C.I. Food Red 7), Ponceau 6R (C.I. Food Red 8), Scarlet GN (C.I. Food Red 2) and erythrosin. (*Cf. Anal. Abstr.*, 1959, **6**, 3202.) J. I. M. JONES

4357. **Recognition of additives in foodstuffs by ultra-violet spectrophotometry. I. Anti-fermentative agents in wine and jams.** F. De Francesco and G. Margheri (Staz. Sper. Agrar., S. Michele all'Adige, Trento, Italy). *Boll. Lab. Chim. Provinciali*, 1961, **12** (1), 5–11.—Anti-fermentatives in wine and jam are identified by u.v. spectrophotometry of suitable extracts. Tannins in wine, and flavourings and hydroxymethylfurfuraldehyde in jam, may also be extracted and can therefore interfere. *Procedure for wine*—Acidify the sample (10 ml) with H_2SO_4 (1:3) (1 ml) and extract with $CHCl_3$ (25 ml) by shaking for 30 min. Three such extractions remove the anti-fermentative agents completely. Plot the extinction between 200 and 300 mμ of the combined extracts against a similar extract of an untreated red or white wine. The anti-fermentative agent is identified from its absorption maximum (tabulated for 18 compounds). *Procedure for jam*—Dissolve the sample (20 g) in boiling H_2O, dilute to 100 ml, filter, acidify with dil. H_2SO_4 (5 ml) and extract with $CHCl_3$ (20 ml). Plot the extinction as described above. Hydroxymethylfurfuraldehyde, when present, will show a peak at 280 mμ, which is sufficiently far removed from the absorption maxima of the added agents not to interfere with their identification. Interference from flavourings is only slight. J. I. M. JONES

4358. **Spectrophotometric determination of caffeine in roasted coffee.** L. Polzella (Lab. Chim. Comunale, Roma, Italy). *Boll. Lab. Chim. Provinciali*, 1961, **12** (1), 23–29.—*Procedure*—Heat the sample (2 g) under reflux in H_2O (100 ml) for 30 min. Cool, and replace any loss of H_2O. Filter and extract 50 ml with $CHCl_3$ (50 ml) after adding 33% NaOH soln. (7 to 8 drops). Filter the extract and transfer 25 ml to a separating-funnel with 33% NaOH soln. (3 to 4 drops) and 0·1N-$KMnO_4$ (10 ml). Shake well, separate and filter the $CHCl_3$ layer, evaporate 10 ml to dryness at 80° to 85°, dissolve the residue in H_2O (50 ml) and make up to 200 ml. Measure the extinction at 274 mμ and calculate the caffeine, taking $E^{1\%}_{1cm}$ for caffeine as 525. For de-caffeinised products use 10 g of material and 20 ml of the $KMnO_4$-treated $CHCl_3$ extract. The caffeine content (%) is then (E × 100)/525; 100% recovery is achieved and the results agree with those by other less rapid methods. The time required is 90 min. J. I. M. JONES

4359. **Detection of added alcohol or sugar in wines. Comparison of the method of Rebelein with that of Seith.** A. Blumenthal (Chem. Lab., Zürich, Switzerland). *Mitt. Lebensmitt. Hyg., Bern*, 1961, **52** (1), 59–65.—Seith's method is based on the determination of the sugar-free extract and the original sugar content, from which an extract number is calculated. Rebelein's method (*Z. Lebensmitt. Untersuch.*, 1957, **105**, 296) is based on the determination of the glycerol[3] and butane-2,3-diol contents, from which a constant *k* is calculated. Seith's method is preferred since it is simpler and more rapid. With it, wines can be classified into three groups—(*i*) those with no added sugar or alcohol; (*ii*) those with added sugar and alcohol; (*iii*) those with no definite indication. Rebelein's method when applied to group (*iii*) may allow more specific classification. R. CLARKE

4360. **Determination of bromoacetates in wine by biological methods.** C. Zambonelli (Ist. Microbiol. Agrar., Univ. Bologna, Italy). *Boll. Lab. Chim. Provinciali*, 1961, **12** (1), 12–22.—Biological methods for detecting preservatives in wine depend on the inhibition of growth of yeast cells, in the presence of suitable nutrients, when the wine is diluted to such a degree as to eliminate inhibition of growth by the alcohol present. Investigations on the detection of bromoacetic acid and its esters show that amounts of < 1 mg per litre are not detectable, and also that these compounds decompose with time, so that eventually they lose all preservative power and are not revealed by the biological method. J. I. M. JONES

4361. **Detection of alkali treatment in animal fats, especially lard. I. Limitation of the method specified by the German meat-inspection law.** R. Engst (Inst. f. Lebensmitt.-chem. beim Magistrat von Gross-Berlin). *Nahrung*, 1961, **5** (2), 164–174.—It was found that while positive reactions in the *p*-nitrophenol and phenolphthalein tests are definite indications of alkali treatment, negative reactions did not prove the absence of alkaline treatment in some instances. Traces of protein and ammonium ions were found in aq. extracts of non-treated lards. Definite proof of alkaline treatment can be obtained neither by the determination of free fatty acid nor by the detection of soap.

II. Flame-photometric determination of alkali in lard. H. Konrad. *Ibid.*, 1961, **5** (2), 175–185.—The official method has been found unreliable and a flame-photometric method for the direct determination of K and Na is described. A Zeiss photometer Model III, equipped with a scale galvanometer, was used. Standard curves for Na and K in the range 1 to 3·5 mg per 100 ml are given. The nephelometric method of Wickboldt (*Angew. Chem.*, 1957, **69**, 530) was used to determine Cl. The calculated equiv. Na was subtracted from the total Na to give "residual" Na. It is thus possible to detect alkaline treatment even in neutralised or acidified fats. I. DICKINSON

4362. **Characteristics of national [Spanish] olive oil. Data from Andalusia. III. Bellier index and its use as a criterion for differentiation.** J. Gracian and G. Arévalo (Inst. de la Grasa, Seville, Spain). *Grasas y Aceites*, 1960, **11** (6), 261–269.—The Bellier indices (temp. of pptn. of the acids of the oil from 70% aq. ethanol) of 265 samples of Andalusian olive oil collected over 4 seasons have been measured. The over-all average value was 6·5°, but individual variations ranged from 2° to 12°. There was less spread of values for each season, probably related to the maturity of the fruit. The index could be considered as a criterion of oil purity only for samples of the same origin and of the same season. L. A. O'NEILL

4363. **Fatty-acids analysis by high-resolution nuclear-spin resonance. A preliminary evaluation.** W. H. Storey, jun. (S. W. Res. Inst., San Antonio, Texas). *J. Amer. Oil Chem. Soc.*, 1960, **37** (12), 676–678.—The high-resolution nuclear-spin resonance spectra of the methyl esters of 9,12,15-linolenic, 9,12-linoleic, 9-oleic and stearic acids in CCl_4 have been produced, and the use of this method for the analysis of an 8-component system resulting from the hydrogenation of linolenic acid has been examined. A Varian Associates V–4311 high-resolution NSR spectrometer is used, which operates at 60 Mc/s, the polarising magnetic field being scanned at 18·6 milligauss per min. The experimental conditions for the reproduction of the relative intensities of the spectral bands have still to be determined. It is shown that if one of the constituents of the mixture other than 9- or 12-oleic acid can be determined by another technique, the application of the nuclear-spin resonance method to the analysis of the remaining mixture is possible. G. R. WHALLEY

4364. **Quantitative determination of steam-volatile fatty acids by gas - liquid chromatography.** C. W. Gehrke and W. M. Lamkin (Dept. of Agric. Chem., Univ. of Missouri, Columbia, U.S.A.). *J. Agric. Food Chem.*, 1961, **9** (1), 85–88.—A modification of the James and Martin procedure (*Biochem. J.*, 1952, **50**, 679) is described for application to biological materials. A soln. of the sodium salts of the acids ($\simeq$ 4 milli-equiv.) is obtained from a steam-distillate or by solvent extraction, with final evaporation on a steam bath. Water (1 ml) is added to the residue, the solution is cooled to 0° and 0·4 ml of conc. H_2SO_4 (at 0°) is added. The soln. is transferred to a 7-mm column packed with 7 cm of Celite 545 over 12 cm of 20 to 40-mesh anhyd. $CaSO_4$ (both previously dried at 300°), and ethyl ether (in small portions) is added until 15 ml of eluate is obtained, collection being made in a tube designed to facilitate subsequent concentration. Removal of water by this procedure is complete. The eluate is evaporated to < 2 ml at $-50°$ and 6 torr, and diluted, at room temp., to 2 ml with dried ethyl ether. A 20-μl aliquot is run in a column similar to that of James and Martin (*loc. cit.*), with suitable instrumental conditions, and thermal-conductivity detection. Evaluation of peaks and areas is carried out with the aid of standard mixtures of pure acids. Recovery of individual acids in synthetic mixtures from acetic to valeric acids usually differed from the actual by $< 10\%$. The procedure may be readily adapted to methyl esters by treating the acids with diazomethane after the final concentration step. C. L. HINTON

4365. **Rapid preparation of fatty acid esters for gas-chromatographic analysis.** L. D. Metcalfe and A. A. Schmitz (Armour Industrial Chemical Co., McCook, Ill., U.S.A.). *Anal. Chem.*, 1961, **33** (3), 363–364.—A BF_3 - methanol reagent is suggested for the conversion of fatty acids into their methyl esters. *Preparation of the reagent*—Weigh 1 litre of methanol in a 2-litre flask, cool it in an ice bath, then bubble BF_3 slowly into the methanol until 125 g is taken up. The reagent is stable for at least 4 months. *Procedure for esterification*—Weigh 100 to 200 mg of fatty acid into a test-tube and add 3 ml of the reagent. Boil for 2 min. on a steam bath. The resulting esters are recovered by simple physical separation of phases after mixing with water (acids containing < 10 C atoms), or by extraction with light petroleum (acids containing > 10 C atoms). A quantitative recovery was not attempted, but the free fatty acid remaining in the esters was $< 1\%$. With care, the recovery can be $> 90\%$. The esters are subjected to gas-chromatographic analysis in the usual way. The method is rapid and is designed for routine determinations of the fatty acids in biological materials, with a sample size ranging from 1 mg to 5 g. R. A. HENDEY

4366. **Thin-film chromatography in the field of vitamins.** E. Nürnberg (Pharm. Entwicklungslab., E. Merck A.-G., Darmstadt, Germany). *Dtsch. ApothZtg*, 1961, **101** (10), 268–269.—To separate pyridoxal (**I**), pyridoxol and pyridoxamine, convert **I** into the methyl acetal by heating under reflux for 1 hr. with methanol, and submit the resulting mixture to thin-film chromatography on a plate of Kieselgel G, first with acetone and then with acetone - dioxan - 25% aq. NH_3 (9:9:2) as developing solvents; dry the plate and spray with 0·4% methanolic 2,6-dibromo-*p*-benzoquinone-4-chlorimine soln. (**II**). To determine the hydrochloride of **I** in a multi-vitamin preparation, convert it into the methyl acetal, precipitate the tetraphenylboron salt, dissolve it in acetone, and submit a 0·2-μg portion to thin-film chromatography

with a 1% soln. of ethanol in $CHCl_3$ as developing solvent and **II** as spray reagent; compare the coloured spot with suitable standards.

A. R. ROGERS

4367. **A new vitamin-A colour reaction.** R. G. Craig, L. M. Bergquist and R. L. Searcy (Dept. of Path., County Osteopathic Hosp., Los Angeles, Calif., U.S.A.). *Anal. Biochem.*, 1960, **1** (4–5), 433–436.—To 50 μg of vitamin A dissolved in 0·5 ml of $CHCl_3$ add 6 ml of acetic acid saturated with $FeSO_4.7H_2O$ and then 2 ml of conc. H_2SO_4, with stirring. A blue colour changing to bright pink is obtained. The max. absorption is at 520 mμ, with lesser peaks at 380 and 440 mμ. The colour reaches a maximum in 2 min. and is stable for 12 min., with slow fading thereafter. The max. colour is given in soln. containing 25% of H_2SO_4. Beer's law is obeyed up to 100 μg of vitamin A and the extinction coeff. is 550. β-Carotene gives a colour with a peak at 740 mμ.

F. POWELL

4368. **Determination of vitamin D in oil solutions.** J. Piekarska and J. Kowalski (Dept. of Hyg. Nourishment, Med. Acad., Warsaw, Poland). *Roczn. Zakl. Hig., Warsaw*, 1960, **11** (6), 515–522.—The method is based on the photometric determination of calciferol after saponification of the oil and purification of the calciferol on activated talc. *Procedure*—Saponify 2 g of the test soln. with 2N-ethanolic KOH (50 ml) on a boiling-water bath for 15 min., cool and extract with ethyl ether (3 × 40 ml). Wash the extract with 5% KOH soln. (40 ml) and H_2O until the washings are neutral to phenolphthalein and dry with anhyd. Na_2SO_4. Evaporate off the ether *in vacuo*, dissolve the residue in $CHCl_3$ (20 ml) and add activated talc to form a semi-liquid mass, mix and set aside for 2 min. Filter off the talc on a sintered-glass filter (3G3) and wash with $CHCl_3$. To 1 ml of the $CHCl_3$ soln. add 6 ml of 20% $SbCl_3$ in $CHCl_3$, containing 2% of acetyl chloride, and after 4 min. measure the extinction in a Pulfrich photometer with S50 filter. Refer the result to a calibration curve prepared by the same procedure.

B. K.

4369. **Chromatography of some lipids on polytetrafluoroethylene [Teflon].** A. C. Arcus and G. G. Dunckley (Nutrit. Res. Dept., Med. Sch., Dunedin, N. Zealand). *J. Chromatography*, 1961, **5** (3), 272–273 (in English).—Previously reported studies on the chromatographic separation of vitamins A and D and cholesterol, on silicone-treated kieselguhr and polyethylene powder columns (Dunckley and Macfarlane, *J. Sci. Food Agric.*, 1955, **6**, 559; Arcus, *Anal. Chem.*, 1959, **31**, 1618), have been extended with Teflon as column medium.

G. P. MITCHELL

4370. **Chromatographic separation of vitamin A and vitamin D.** H. Daniëls, A. H. J. Gijzen and A. W. M. Indemans (Lab. Ned. Apoth., Utrecht, Netherlands). *Pharm. Weekbl.*, 1961, **96** (3), 91–105.—*Procedure*—Saponify 100 to 300 mg of sample with ≃ 100 mg of quinol and 10 ml of N-ethanolic KOH and mix the cooled hydrolysate with 25 ml of benzene until a homogeneous soln. is obtained. Extract the saponified material first with 10 ml of N-KOH and then with 10 ml of 0·5N-KOH, finally washing the benzene phase with water (4 × 10 ml) until the washings are neutral to phenolphthalein. Dry the benzene soln. Evaporate an aliquot of this soln., containing at least 200 i.u. of vitamin D, to dryness at ≯ 50° under CO_2, and dissolve the residue in ≃ 2 ml of light petroleum. Transfer this soln. to a column (25 cm × 2 cm) containing 12·5 g of Celite 545 and 10 ml of polyoxyethylene glycol 600 in light petroleum, elute with light petroleum, collect the 10 to 30-ml fraction, evaporate it to dryness at ≯ 50° under CO_2 and dissolve the residue in 2 ml of light petroleum (soln. *A*). Then elute vitamin A with ≃ 80 ml of light petroleum, checking that the elution is complete with the aid of u.v. light. Dilute the eluate with abs. ethanol to a concn. of 5 to 15 i.u. per ml and determine vitamin A spectrophotometrically (Morton and Stubbs, *Analyst*, 1946, **71**, 348). Transfer soln. *A* to a column (20 cm × 0·5 cm) containing a suspension of 2 g of Floridin in 10 ml of light petroleum, wash the column with light petroleum (4 × 5 ml), elute with benzene and collect exactly 10 ml. To a 1-ml aliquot, containing 200 to 400 i.u. of vitamin D, add 3 ml of $SbCl_3$ soln. prepared according to de Witt and Sullivan (*Ind. Eng. Chem., Anal. Ed.*, 1946, **18**, 117), and measure the extinction at 500 mμ at six 1-min. intervals after the addition of the reagent and at 550 mμ after 0·5 min. and then at five 1-min. intervals after the addition of the reagent. Determine the extinction at zero time by extrapolation (*cf.* Rogers, *J. Pharm. Pharmacol.*, 1954, **6**, 780; *Ibid.*, 1955, **7**, 731; and Stross and Brealey, *Ibid.*, 1955, **7**, 739).

M. J. MAURICE

4371. **Determination of vitamins in cereals and cereal products.** J. Janicki and E. Kaminski (Landwirtschaftl. Hochsch., Poznan, Poland). *Getreide u. Mehl*, 1961, **11** (1), 1–7.—Twenty-one laboratories have analysed the same wheat and wheat flour to determine their thiamine, riboflavine and PP-factor contents by agreed chemical and microbiological methods and also by slight variations of these methods. Averages and spread of results thus obtained are tabulated. The thiochrome method is recommended for the determination of thiamine, and either a chemical or microbiological method for the PP factor. The lumiflavine method gives higher values than the fluorimetric or microbiological methods for riboflavine. (48 references.)

J. V. RUSSO

4372. **Determination of ascorbic acid. Study of the method of Roe and Kuether and some modifications.** J. A. Santome and R. F. Banfi. *Rev. Asoc. Bioquim. Argentina*, 1961, **25**, 84–94.—The Roe and Kuether method for the determination of ascorbic acid (*J. Biol. Chem.*, 1943, **147**, 339), and various modifications, all of which depend on the oxidation of the ascorbic acid, followed by formation of an osazone with 2,4-dinitrophenylhydrazine, determined photometrically, have been compared by using various photometers and spectrophotometers. The original method was generally preferred.

L. A. O'NEILL

4373. **Determination of total vitamin E and individual tocopherols in animal and vegetable protein-containing materials.** H. Kubin and H. Fink (Inst. f. Gärungswiss. u. Enzymchem., Univ., Köln, Germany). *Fette, Seif., Anstrichmitt.*, 1961, **63** (3), 280–286.—The presence of carotenoids, sterols and other substances which are easily oxidised can interfere seriously with the determination of vitamin E. The preparation of the sample, saponification, extraction, the removal of

interfering substances and the interpretation of results are discussed. Two paper-chromatographic methods for the determination of total tocopherols and a column-chromatographic method for the determination of individual tocopherols are described. Results for various protein-containing substances are given. I. DICKINSON

See also Abstracts—**4206**, Kjeldahl determination of N. **4251**, Determination of maltol. **4281**, As and Sb in foods. **4296**, Thiamine and its phosphates in tissues. **4311**, Separation of cholesterol fatty esters. **4335**, Determination of folic acid. **4381**, Gibberellins in green malt. **4385**, Crude fibre determination. **4387**, Organo-phosphorus residues in foodstuffs. **4399**, Oxidative stability of lipids.

Sanitation

Analysis of air, water, sewage, industrial wastes, industrial poisons.

4374. **Identification of aliphatic amines in air as their benzamides by paper chromatography.** J. P. Lodge, jun., and E. D. Barber (Air Pollut. Engng Res., Robert A. Taft San. Engng Center, Cincinnati, Ohio, U.S.A.). *Anal. Chim. Acta*, 1961, **24** (3), 235–240 (in English).—After extraction with NaOH and ethyl ether from acid soln., the amines were converted into the amides with benzoyl chloride and separated by paper chromatography. The solvent systems 80% methanol - cyclohexane (1:4) and 20% propanol - cyclohexane (1:4) were satisfactory, and a table of R_F values is given. The use of radioactive benzoyl chloride increased the sensitivity of the method. P. D. PARR-RICHARD

4375. **Colorimetric determination of chlorine dioxide in water.** A. T. Palin (Newcastle and Gateshead Water Co., Newcastle upon Tyne, England). *Wat. & Sewage Wks*, 1960, **107** (12), 457–458.—*Procedure*—The sample of water (100 ml) is mixed with KI (a few crystals) and 5% (v/v) H_2SO_4 (1 ml), and, after setting aside the soln. for 1 min., *p*-amino-*NN*-diethylaniline oxalate or sulphate reagent containing EDTA (prep. described) (0·5 g) and 5% $NaHCO_3$ soln. (4 ml) are added. The red soln. is titrated to a colourless end-point with standard $(NH_4)_2SO_4.FeSO_4$ soln. Modifications for determining free Cl and chloroamines are described. C. A. SLATER

4376. **Determination of trace elements in natural water.** B. F. Mitskevich and E. S. Nazarevich. *Gidrokhim. Materialy*, 1960, **30**, 177–180; *Ref. Zhur., Khim.*, 1961, (4), Abstr. No. 4D117.—Zirconium, Be, Sc, Ga, Ge and other elements can be determined by co-pptn. with $Al(OH)_3$, since their hydroxides formed in alkaline - ammoniacal medium have similar properties. Owing to the capacity of $Al(OH)_3$ to adsorb quant. coloured metal sulphide particles (formed by the addition of Na_2S), such metals as Ni, Co, Pb and Sn can be determined at the same time as the rarer elements, and by the same method. The method is simple and sensitive and particularly useful for determining elements not extractable with dithizone. K. R. COOK

4377. **Determination of dissolved radium [in public water-supplies].** A. S. Goldin (Robert A. Taft San. Engng Center, Cincinnati, Ohio, U.S.A.). *Anal. Chem.*, 1961, **33** (3), 406–409.—The procedure given permits determination of concn. of ^{226}Ra as low as 5×10^{-9} μC per ml. *Procedure*—To the sample add M-citric acid (5 ml) and make the soln. alkaline with aq. NH_3. Add aq. N-$Pb(NO_3)_2$ (2 ml) and 0·1N-$Ba(NO_3)_2$ (1 ml) as carriers, heat the soln. to 100° and precipitate the Ra plus carriers with H_2SO_4 (1:1) at pH 1. Collect the ppt., wash it twice with conc. HNO_3, dissolve it in 0·25M-EDTA (disodium salt), and then re-precipitate the $BaSO_4$ by dropwise addition of glacial acetic acid in excess. Wash the ppt. of $BaSO_4$ and determine the amount of Ra therein by α-counting. The sensitivity is $\simeq 10^{-12}$ g of Ra and the reproducibility is $\simeq \pm 10\%$. The masking by EDTA assures high decontamination from other α-emitters and from the Pb carriers. Improvements over earlier procedures (DeSesa, *U.S. Atomic Energy Comm.*, 1958, WIN-101; Jenkins and Sneddon, A.E.R.E. Report C/R 2385, 1953) are claimed. The concn. of ^{223}Ra, ^{224}Ra and ^{226}Ra can be determined separately by measurements of ingrowth and decay. W. J. BAKER

4378. **The co-crystallisation of ultra-micro quantities of molybdenum with benzoin α-oxime. Determination of molybdenum in sea water.** H. V. Weiss and M. G. Lai (U.S. Naval Radiological Defence Lab., San Francisco, Calif., U.S.A.). *Talanta*, 1961, **8** (2–3), 72–76 (in English).—The addition of a soln. of benzoin α-oxime in acetone to an aq. soln. containing traces of Mo, followed by the evaporation of most of the acetone, results in the co-pptn. of the Mo - benzoin α-oxime compound with the slightly soluble benzoin α-oxime. Quantitative recoveries of Mo were obtained when 120 to 200 mg of benzoin α-oxime in 5 ml of acetone was added to $\simeq$ 10 ml of a soln. containing ^{99}Mo (γ-activity 10^5 to 10^6 counts per min.), provided that the pH was in the range 1·8 to 5·5. A procedure for the separation of Mo from sea water, and for its subsequent colorimetric determination by means of thiocyanate, has been devised. The Mo content of a sample of sea water was found to be 12·2 ± 0·1 μg per litre. R. M. ROWLEY

4379. **Determination of alkylbenzenesulphonates in sewage.** Analytical Subcommittee of the Technical Advisory Council, Association of American Soap and Glycerine Producers, Inc. *J. Wat. Pollut. Control Fed.*, 1961, **33** (1), 85–91.—After being extracted from the sewage sample and purified, the alkylbenzenesulphonate is converted into the 1-methylheptylamine salt, and quantitatively identified by comparing a spectrum of an evaporated film (2 to 15 μ) with a similar standard spectrum. Quantitative data are obtained by comparing intensities of the 9·6-μ and 9·9-μ infrared absorption bands with a calibration curve prepared by using known amounts of standard sample. B. F. FULLAN

4380. **Comparative studies on the determination of zinc in sewage wastes.** W. Dożańska and H. Czarnodolowa (Dept. of Communal Hyg., State Inst. of Hygiene, Warsaw, Poland). *Roczn. Zakl. Hig., Warsaw*, 1960, **11** (4), 313–325.—Six methods were compared. A modified EDTA method was found to be the best. *Procedure*—To an aliquot (containing 1 to 10 mg of Zn) of the mineralised sample add an excess of aq. NH_3 (to pH $\simeq$ 10), filter off the pptd. hydroxides of Fe and Al and wash them with hot ammoniacal H_2O. Dissolve the

ppt. in HCl, wash the filter with hot H_2O, collect the filtrate in the original flask, re-precipitate, collect the ppt. on the same filter and wash several times with hot H_2O. Boil the combined filtrates with 0·01 g of ascorbic acid, cool, add 10 ml of aq. NH_3 - ammonium acetate buffer (to pH 9 to 10) and 5% aq. KCN (10 ml) to convert the Zn and Cu into cyanide complexes. Add 0·5% Eriochrome black T soln. in 96% ethanol (0·3 to 0·4 ml per 100 ml) and titrate the sum of Ca, Mg, Pb and Mn with 0·01M-EDTA (disodium salt). Add 10 ml of 4% formaldehyde soln. to liberate Zn from its complex and titrate with 0·01M-EDTA (disodium salt). A modification is described in which Fe is masked with triethanolamine. B. K.

See also Abstracts—**4094**, Borane in air. **4232**, Trichlorosilane in air. **4398**, Analyser for H, CH_4 or acetone in air. **4431**, Trace elements in sea water.

Agricultural analysis

Soil, fertilisers, herbicides, pesticides, animal feeding-stuffs.

4381. **Determination of endogenous gibberellins in green malt by isotopic derivative dilution procedures.** L. Lazer, W. E. Baumgartner and R. V. Dahlstrom (Phys. Chem. Dept., Abbott Lab., North Chicago, Ill., U.S.A.). *J. Agric. Food Chem.*, 1961, **9** (1), 24–26.—Tritium-labelled gibberellic acid and ^{14}C-labelled diazomethane were used in procedures for the determination of endogenous gibberellic acid (**I**) in sprouting barley. The results varied rather widely according to minor experimental variations. It is suggested that the **I** was present in a predominantly bound form capable of liberating free **I** either by a mild acid treatment or by a pH-sensitive enzymatic reaction. C. L. HINTON

4382. **Determination of saponins in alfalfa [lucerne].** G. R. Van Atta, J. Guggolz and C. R. Thompson (W. Reg. Res. Lab., Agric. Res. Service, U.S. Dept. of Agric., Albany 10, Calif.). *J. Agric. Food Chem.*, 1961, **9** (1), 77–79.—A reasonably rapid procedure is described. The dried coarsely ground or chopped sample (15 g) is mixed with water (75 ml) and set aside for 5 hr.; ethanol (95%) (210 ml) is added and mixed in, and the flask is stoppered and left for 20 hr. Ethanol (95%) (53 ml) and water (162 ml) are then added, and after 1 hr. the mixture is filtered, with suction, through paper. Activated carbon (1 g) is added to the filtrate (50 ml), the mixture is warmed over steam with occasional stirring for 15 min. and filtered. The filtrate and aq. ethanolic washings are evaporated almost to dryness over steam, the residue is dissolved by warming with water (20 ml) and the soln. is re-treated with carbon (1·5 g) and re-filtered. The carbon is washed successively with water (4 × 20 ml), ethanol (10%) (2 × 20 ml) and ethanol (20%) (2 × 20 ml), the filtrates and washings being discarded. The saponins are then eluted by washing the carbon with pyridine - ethanol (3:7) (200 ml). Throughout filtration and elution the liquid level must be held above the filter cake. The eluate is evaporated in a tared dish, the residue is dried under vacuum at 65° for 16 hr., and weighed as saponins. Results are probably somewhat high, but are sufficiently accurate for studies of the occurrence of saponins in lucerne and their significance in animal diets. Commercial activated carbons differ in suitability for the procedure, and each lot to be used must be selected by tests (described) on a known preparation of lucerne saponins. C. L. HINTON

4383. **Rapid procedure for estimating potentially available soil nitrogen under greenhouse conditions.** E. R. Purvis and M. W. M. Leo (Soils Dept., Rutgers Univ., New Brunswick, N.J., U.S.A.). *J. Agric. Food Chem.*, 1961, **9** (1), 15–17.—A procedure is described for determining the more readily hydrolysable N fraction in soils. To 1·0 g of air-dried soil (passed through a 1-mm screen) is added 2 ml of 0·2% (v/v) H_2SO_4 soln., and the mixture is dried on a steam bath. Water (50 ml) and 1 drop of 5% $Na_2PO_4.12H_2O$ soln. are added, and the mixture is stirred thoroughly and filtered through a Whatman No. 2 paper (previously washed free of NH_3 with 0·5% NaCl soln.). A 5-ml aliquot of the filtrate is treated with 0·2 ml of Nessler's reagent and the transmittance at 420 mμ is determined after 20 min. and referred to a standard curve prepared from soln. containing 1 to 5 p.p.m. of ammonia-N. In experiments with wheat germ, good correlation was found between the N released by the method described, and the N-supplying power of the soils. C. L. HINTON

4384. **Method for the determination of the nitrogen content of ammonium nitrate - chalk [nitrochalk].** B. Enyedi, G. Bencz and F. Bagyinszky (Chemical Works, Kazincbarcika, Hungary). *Magyar Kém. Lapja*, 1961, **16** (3), 131–134.—In the method described, the ammonia-N and nitrate-N are determined separately and the total N is obtained by addition. The error is within ± 1%. The ammonia-N is determined by reaction of the ammonium salts with neutral formaldehyde; the liberated acid is titrated with standard NaOH soln. The nitrate-N is determined by reduction of the nitrate by a known excess of standard $FeSO_4$ soln., followed by back-titration with standard $KMnO_4$ soln. The determination of nitrate-N by dead-stop titration is also described. The nitrate is reduced by $(NH_4)_2SO_4.FeSO_4$ in H_2SO_4 medium. B. VASZKO

4385. **Semi-micro technique for crude fibre determination.** R. M. Bredon and C. D. Juko (Animal Health Res. Centre, P.O. Box 24, Entebbe, Uganda). *J. Sci. Food Agric.*, 1961, **12** (3), 196–201.—A rapid method suitable for routine work is described. *Procedure*—Weigh 0·25 to 0·30 g of the dried, milled and defatted sample into a 50-ml silica tube, add 25 ml of 1·25% (v/v) H_2SO_4 to each tube and immerse in a water bath which is heated to boiling within 10 min. Add a further 1 ml of acid and continue boiling for a further 40 min., shaking the tubes occasionally. Remove the tubes and centrifuge. Remove the supernatant liquid, wash the residue with hot water and centrifuge again (5 min. at 3500 r.p.m.). Repeat the procedure with 1·25% NaOH soln., wash the residue twice, dry the tubes at 105° for 8 hr., cool in a desiccator and weigh. Ignite at 600°, cool and re-weigh. Correct for the fat content. The semi-micro technique gave a higher standard deviation than the standard method, but the difference between the results is ≯ 3%. I. DICKINSON

4386. **Determination of tetracyclines in feeding-stuffs with uranyl nitrate as reagent.** H. Tschapke (Inst. f. Ernährung, Potsdam-Rehbrücke, Berlin,

Germany). *Ernährungsforschung*, 1960, **5** (5), 551–557.—The method described is suitable for the determination of tetracycline, and oxy- and chlortetracyclines. The feeding-stuff concentrate (0·5 to 2 g) is defatted with ether (either in a Soxhlet apparatus or in a centrifuge tube), then the residue is extracted by shaking for 40 min. with acetone - H_2O - 88% formic acid (14:5:1). The mixture is centrifuged for 5 min. and the clear extract is made up to 50 ml with the extracting soln. A 25-ml portion is mixed with 1 ml of 20% uranyl nitrate soln. and the extinction of the yellow colour is measured against a reagent blank at 365 mμ. Equations are given for the calculation of each tetracycline. The determinable range is 50 to 1500 μg of tetracycline in 10 ml. J. V. Russo

4387. **Determination of residual organophosphorus insecticides in foodstuffs. A review.** E. D. Chilwell and G. S. Hartley (Fisons Pest Control Ltd., Chesterford Park Res. Sta., Essex, England). *Analyst*, 1961, **86**, 148–159.—After an introductory discussion of the nature of the problems involved in the determination of insecticide residues, the general procedures available for extraction of the insecticide, its separation from possible interfering substances and its subsequent determination are reviewed. Methods available for the determination of 19 individual insecticides are briefly summarised. (72 references.) A. O. Jones

4388. **Fluorimetric method for estimation of residues of Bayer 22,408 [*OO*-diethyl O-naphthalimidophosphorothioate].** P. A. Giang (Entomol. Res. Div., Agric. Res. Service, U.S. Dept. of Agric., Beltsville, Md.). *J. Agric. Food Chem.*, 1961, **9** (1), 42–44.—The method described, suitable for determining microgram amounts of this insecticide in milk, butter fat and plant material, is based on the fluorescence shown by this compound in methanolic NaOH, which is greatly enhanced when dioxan containing a little H_2O_2 is added to the reaction mixture. A suitable amount of the $CHCl_3$ soln. of the extracted material (purified chromatographically as described) is freed from solvent on a steam bath, then 0·1N-methanolic NaOH (2 ml) is added. After 5 min., dioxan reagent (100 ml of dioxan plus 1 ml of 30% H_2O_2 soln.) (10 ml) is added and the mixture is filtered through 1 g of anhyd. Na_2SO_4 in a Whatman No. 2 paper. The filtrate is examined in a fluorimeter, adjusted to 100% transmittance with quinine sulphate soln. (4 μg and 1·33 μg per ml in the reference and sample beams, respectively). The reading is referred to a standard curve prepared from a $CHCl_3$ soln. containing 1 mg of the insecticide per 100 ml.
C. L. Hinton

4389. **Modified Schöniger combustion for determination of residues of arsenic, bromide, chloride, manganese and nickel in pesticide-treated plant material.** W. H. Gutenmann, L. E. Saint John, D. L. Barry, E. D. Jones and D. J. Lisk (Dept. of Entomology, N.Y. State Coll. Agric., Cornell Univ., Ithaca, N.Y.). *J. Agric. Food Chem.*, 1961, **9** (1), 50.—The procedure previously described (Gutenmann and Lisk, *Anal. Abstr.*, 1961, **8**, 1721) for the combustion of plant materials in a 5-litre flask has been extended to the determination of residues of arsenic in potatoes, inorganic bromide in cherries, inorganic chloride in potatoes, maneb (Mn ethylene-1,2-bisdithiocarbamate) in cabbage and onions, and a nickel-containing fungicide in oats. The subsequent procedure for these constituents is briefly described. C. L. Hinton

4390. **Decline and residue studies on 4-chlorobut-2-ynyl *m*-chlorophenyl carbamate [barban].** J. R. Riden and T. R. Hopkins (Spencer Chemical Co., Kansas City, Mo., U.S.A.). *J. Agric. Food Chem.*, 1961, **9** (1), 47–49.—Rapid disappearance of the herbicide barban, used for the control of wild oats in wheat, etc., was found when the green plants were examined after treatment, and residues of < 0·01 p.p.m. were found in the ripe food portions of the crops. For the determination, green tissue is chopped and ground in a high-speed mixer with 1,2-dichloroethane (**I**) to a thin paste, which is filtered through glass wool; the tissue is reprocessed with **I** and then washed twice with **I**. For beet and peas, isopropyl alcohol or methyl cyanide is used, with filtration through cheesecloth. Grain is homogenised with **I** in the mixer, and **I** and the washings are removed by centrifuge. Interfering substances are removed on a column (30 mm × 500 mm or 20 mm × 300 mm according to size of sample) of Celite - anhyd. Na_2SO_4 - Attaclay (1:2:2), supported on 1 in. of sand on glass wool. The extracts are first passed through, then the successive washings and finally fresh **I**. The combined percolates are evaporated at 30° to 50° and the residue is heated under reflux for 1 hr. with 100 ml of 10% NaOH soln. The resulting *m*-chloroaniline is steam-distilled into 5 ml of N-HCl, until about 40 ml is obtained, and treated with 1% KNO_2 soln. (1 ml), 2% ammonium sulphamate soln. (1 ml) and 0·1% *N*-1-naphthylethylenediamine dihydrochloride soln. (1 ml). After 20 min., 5 ml of 6N-HCl is added, the soln. is made up to 50 ml, and the extinction at 550 mμ is measured. Background extinction, due, for example, to the extracted green plants, should be determined and allowed for. With older plants, interference may be caused by alkaline hydrolysis of tryptophan; a chromatographic procedure for dealing with this is described. C. L. Hinton

---

See also Abstract—**4246**, Triphenyltin acetate in plants.

5.—GENERAL TECHNIQUE AND APPARATUS

General

4391. **Paper for modern chemical analytical procedures.** A. Grüne (C. Schleicher & Schüll, Dassel, Germany). *Öst. ChemZtg*, 1961, **62** (3), 74–81.—A review is presented of the types of paper available for several analytical techniques. The applications considered include conventional filtration with ordinary, hardened, glass- and P.V.C.-fibre filters, paper chromatography, paper electrophoresis, spot reactions and the ring oven, column chromatography with cellulose powder and ion exchange with cellulose-based exchangers. (27 references.) W. T. Carter

4392. **Automatic operation of glass stopcocks.** F. O. Anderson and L. R. Crisp (Instr. Engng and Devel. Branch, Div. of Res. Services, Dept. of Health, Educ. and Welfare, Bethesda, Md., U.S.A.). *Chemist Analyst*, 1961, **50** (1), 22.—Glass stopcocks with fluorocarbon barrels are opened and closed without shock by means of shafts actuated by two solenoids. The solenoid circuit is appropriately triggered (*e.g.*, by electrical timing, liquid level or optical systems) according to the application of the unit. The apparatus is reliable and inexpensive and acts rapidly. J. H. Waton

4393. **An inexpensive null-reading torsion balance.** D. L. Kraus, A. W. Petrocelli and J. C. Price (Dept. of Chem. and Pharm., Univ. of Rhode Island, Kingston, U.S.A.). *Anal. Chem.*, 1961, **33** (3), 479–480.—An easily constructed, inexpensive balance for *in situ* vacuum or dry-box weighings in the milligram to gram range is described. The balance is sturdy and reliable. C. B. BAINES

4394. **Automatic recording balance.** Z. Kučerovský, F. Říha and I. Slavíček (Res. Inst. Macromol. Chem., Brno, Czechoslovakia). *Chem. Průmysl*, 1961, **11** (3), 137–139.—The arrangement described enables the samples to be weighed in the ranges of 0 to 10 mg or 0 to 5 mg with an accuracy of ± 1% or ± 2%, respectively. J. ZÝKA

4395. **Construction, calibration and use of a modified quartz-fibre "fishpole" ultra-micro balance.** S. L. Bonting and B. R. Mayron (Dept. Biol. Chem., Univ. of Illinois Coll. of Med., Chicago, U.S.A.). *Microchem. J.*, 1961, **5** (1), 31–42.—Fourteen "fishpole" balances, with sensitivities ranging from 0·27 to 5·0 mμg, were constructed with uncoated silica fibres, 9 to 17 μ in diameter, which had become commercially available. A calibration curve for each balance was constructed by weighing individual crystals of quinine hydrobromide; curves for 4 balances are shown as examples. In every case, a linear relationship was obtained between deflection and load, and the observed sensitivity agreed closely with the calculated value. The reproducibility for replicate weighings was good (the mean coeff. of variation was 1·11%) and varied little with the sensitivity of the balance. Young's modulus of elasticity of quartz, determined with these balances, was 5·50 (± 0·139) × 10^9 mg per sq. mm and was independent of fibre diameter. I. A. SIMPSON

4396. **Simple laboratory ultra-micro burette.** A. Ziegelhöffer, M. Hubka and G. Foglsinger (Dept. Exp. Surgery, Inst. Exp. Med., Acad. Sci., Bratislava, Czechoslovakia). *Chem. Zvesti*, 1961, **15** (2), 158–160.—A modification of the Habermann burette (*Chem. Listy*, 1959, **53**, 30) is described. J. ZÝKA

4397. **Apparatus for the storage and delivery of strong reducing titrants.** J. Doležal and J. Zýka (Dept. of Anal. Chem., Charles' Univ., Prague, Czechoslovakia). *Chemist Analyst*, 1961, **50** (1), 20.—The apparatus consists of a titration vessel, burette and a storage unit in which the reductant is prepared and from which it is pumped by the introduction of an inert gas. The titrant is allowed to flow over a reducing packing (*e.g.*, zinc) so that the desired reduction state is achieved without a change in molarity. J. H. WATON

4398. **Continuous gas-analyser based on catalytic combustion on incandescent platinum.** C. Eyraud, B. Domanski, P. Devore and H. Botazzi (Lab. de Chim. Ind., Fac. des Sci., Lyon, France). *Chim. Anal.*, 1961, **43** (3), 136–142.—An apparatus and procedure are described and illustrated for the continuous determination of low concn. (≃ 1%) of H, methane or acetone in air by catalytic oxidation on pre-activated platinum - rhodium (9:1) wires at the requisite temp. (≃ 1100° for methane and 400° for acetone). The wires last continuously for 150 to 250 hr. without damage or loss of activity. Zero drift and change in sensitivity are virtually eliminated by adopting a Wheatstone-bridge arrangement in which the same heated wire acts alternately and successively as combustion and 'reference' arms, the differential measurements being made at such a frequency that the integrator provides a continuous record. The precision and sensitivity are equivalent to those of existing discontinuous analysers, and the time response is almost instantaneous. W. J. BAKER

4399. **Modified recording oxygen-absorption apparatus for the determination of oxidative stability of lipid material.** H. F. Martin (Res. Ass. of British Flour-Millers, Cereals Res. Sta., St. Albans, Herts., England). *Chem. & Ind.*, 1961, (12), 364–367.—The method and apparatus of Sylvester *et al.* (*J. Soc. Chem. Ind., London*, 1942, **61**, 165) is modified so that the sample size can be reduced to 0·1 g. A 4-unit model is still used, but with magnetic stirring instead of shaking, so that an all-glass connection can be made between the reaction flasks and the manometer tubes, and the whole apparatus can be assembled with the recorder as a single unit. There are also some modifications to the water-heating and O-pressure-recording systems. *Procedure*—Samples of fats are dissolved in light petroleum, or, for fat in cereals, the sample is vacuum freeze-dried, and the readings of O-absorption against time are made as previously described (*loc. cit.*). The induction period is not significantly altered by variation in sample size between 0·1 and 1·0 g. By using as substrate an oil of low induction period (≃ 1 hr.), antioxidants can be compared. E. J. H. BIRCH

4400. **Micro-filtration under pressure into a volumetric flask.** J. J. Kolb (Inst. for Cancer Res., Philadelphia, Pa., U.S.A.). *Chemist Analyst*, 1961, **50** (1), 23–24.—The apparatus consists of a Büchner-type sintered-glass filter-funnel of appropriate porosity fitted to a flask, and a syringe the needle of which is inserted into a rubber stopper that fits the funnel. The soln. for filtration is placed in the funnel, and the stopper is inserted with the syringe plunger in the uppermost position. When the plunger is depressed slowly, the filtrate will pass into the flask. J. H. WATON

4401. **Measuring melting-points and rates of crystallisation of polymers by recording changes in birefringence.** C. W. Hock and J. F. Arbogast (Res. Center, Hercules Powder Co., Wilmington, Del., U.S.A.). *Anal. Chem.*, 1961, **33** (3), 462–465.—The rapid method described is applicable to polymer in the form of powder, film or moulded piece. The apparatus automatically and simultaneously measures and records the brightness between crossed Nicols and also the temperature of the specimens. Under the conditions given, the melting-point values are reproducible to better than ± 0·5°. C. B. BAINES

4402. **Apparatus for differential thermal analysis at low temperatures.** I. Proks and V. Šiške (Acad. Sci., Bratislava, Czechoslovakia). *Chem. Zvesti*, 1961, **15** (4), 309–314.—The apparatus enables the linear increase or decrease of the temp. to be maintained exactly and is based on moving a block containing the sample and the standard into or out of a vertical metal tube. The lower part of the block is maintained at a low temp. by a freezing mixture, the upper part is heated in a small furnace. The linear decrease or increase of the temp. is

obtained by regulation of the rate of transfer of the block into and out of the apparatus.

J. ZÝKA

See also Abstract—**4268**, Apparatus for mol. wt. of polymers.

Chromatography, ion exchange, electrophoresis

4403. **Analogue integration techniques in chromatographic analysis.** A. Strickler and W. S. Gallaway (Beckman Instruments, Inc., Fullerton, Calif., U.S.A.). *J. Chromatography*, 1961, **5** (3), 185–193 (in English).—A method of analogue integrating is described which is particularly applicable to gas chromatography, also, in a modified form, to paper chromatography when an automatic integration of an array of spots of variable shape and density is required. The use of this method eliminates pip counting and the need for trigger circuitry. A supplementary ball and disc integrator drives a light-sensitive, self-developing paper past a constantly illuminated slit. The distance between lines produced on this paper ("strip integram" recording) is proportional to the integrated area of chromatogram peaks. G. P. MITCHELL

4404. **Standardisation of silicic acid for chromatography.** R. Hernandez, R. Hernandez, jun., and L. R. Axelrod (Southwest Foundation for Res. and Educ., San Antonio, Tex., U.S.A.). *Anal. Chem.*, 1961, **33** (3), 370–373.—Three procedures are described for the activation and standardisation of silicic acid so that it can be obtained in 10 grades of activity as designated by the Brockmann scale for alumina. Each activity is evaluated from the positions and movement of the six Brockmann dyes used in pairs in a solvent mixture of pentane and benzene (4:1) (*cf.* Brockmann and Schodder, *Ber.*, 1941, **74**, 73). The purity and grade of activity can be consistently reproduced, thus facilitating the column-chromatographic separation of biological compounds on silicic acid.

W. J. BAKER

4405. **A sample applicator for chromatographic paper and its use for 5-hydroxymethyl-2-furaldehyde and laevulic acid analysis.** S. W. McKibbins, J. F. Harris and J. F. Saeman (Forest Prod. Lab., U.S. Dept. Agric., Madison, Wis., U.S.A.). *J. Chromatography*, 1961, **5** (3), 207–216 (in English).—Details of a mechanical device are given, by which a thin continuous line of sample solution is applied reproducibly and uniformly on to a strip of chromatographic paper from a hypodermic syringe. This applicator is successfully used in quantitative chromatographic studies of 5-hydroxymethyl-2-furaldehyde and laevulic acid produced from the acid-catalysed decomposition of glucose. Details of the chemical analytical determination of these two compounds by u.v. spectrophotometry and by the iodoform reaction, respectively, are given.

G. P. MITCHELL

4406. **Chromatographic desalting apparatus.** Baird & Tatlock (London) Ltd. (Chadwell Heath, Essex, England). *Lab. Practice*, 1961, **10** (3), 153–154.—The electrolytic desalting apparatus is based on one described by Blainey and Yardley (*Nature*, 1956, **177**, 83). The anode and cathode compartments are separated from the centre compartment by anion- and cation-exchange membranes. The centre compartment, which contains the soln. to be desalted, has three cells in parallel, of capacities 1, 2 and 3 ml, and arranged so that one or more may be used simultaneously. Whilst all the electrolyte cannot be removed without appreciable loss of amino-acids, the apparatus can be considered as providing a rapid means of reducing the concn. of electrolytes, thus giving a partially desalted soln. that may be chromatographed. A desalting time of 6 min. removed the largest amount of electrolyte (50 to 70%); some 15 to 17% of lysine or arginine was lost, but $\geq$ 7% of other amino-acids. J. H. WATON

4407. **Liquid scintillation counting of radioactive chromatograms.** J. Nunez and C. Jacquemin (Lab. Biochim. Gén., Collège de France, Paris). *J. Chromatography*, 1961, **5** (3), 271–272 (in French).—A previous technique for counting the activity of ^{3}H-labelled compounds in paper chromatograms (Wang and Jones, *Biochem. Biophys. Res. Commun.*, 1959, **1**, 203; Geiger and Wright, *Ibid.*, 1960, **2**, 282) is modified. The new technique involves the impregnation of chromatograms with 2 or 3 drops of the scintillation liquid, giving a greater transparency, then counting directly with a liquid scintillation counter. G. P. MITCHELL

4408. **Preparation of an adsorbent for gas-liquid chromatography.** A. N. Genkin, V. F. Evdokimov, B. I. Boguslavskaya and A. A. Timofeeva. USSR Pat. 133,268 (10.11.1960).—Silicone rubber is deposited on a support and vulcanised by means of radioactive radiation. In an example, 20 g of diatomite brick, grain size 0·25 to 0·35 mm, is moistened with a soln. of 4 g of dimethylsiloxane rubber (mol. wt. 3×10^5) in 100 ml of ethyl ether. The solvent is removed, and the rubber deposited on the support is vulcanised by means of γ-radiation from ^{60}Co (dose $28{\cdot}8 \times 10^{16}$ r.) at 0·72 r. per hr. The brick is then treated with 20% of its wt. of a silicone resin of b.p. 210°. The adsorbent is suitable for the chromatographic separation of fluorohydrocarbons.

C. D. KOPKIN

4409. **Adsorption on the liquid phase in gas chromatography.** R. L. Martin (Res. and Devel. Dept., American Oil Co., Whiting, Ind., U.S.A.). *Anal. Chem.*, 1961, **33** (3), 347–352.—A new equation for retention volumes is given which takes into account the adsorption at the liquid-gas interface. n-Hexadecane, 3,3′-thiodipropionitrile and 1-chloronaphthalene, representing 3 types of liquid phase, are studied, and observed retention volumes show that adsorption on the liquid is most important when the liquid is highly polar and a poor solvent, when the surface area of the support is high, and when the ratio of liquid to support and the temperature are low. With non-polar liquid phases, adsorption on the liquid is less important than adsorption on the support.

C. B. BAINES

4410. **An infra-red gas cell for the direct collection of gas-chromatographic fractions.** S. S. Chang, C. E. Ireland and H. Tai (A. E. Staley Mfg Co., Decatur, Ill., U.S.A.). *Anal. Chem.*, 1961, **33** (3), 479.—The simple, readily constructed cell described allows easy transfer of the sample collected

in a cold trap to a suitable infra-red cell. The uncontaminated sample is also available for further analysis. C. B. BAINES

4411. **Automatic recording of the radioactivity of zones eluted from the gas - liquid chromatogram.** A. T. James and E. A. Piper (Nat. Inst. Med. Res., Mill Hill, London). *J. Chromatography*, 1961, **5** (3), 265–270 (in English).—Present techniques of continuously recording radioactivity of vapours eluted from gas - liquid chromatograms are discussed, and an alternative method is proposed. Argon is used as the carrier gas and all organic compounds issuing from the column are burned over heated CuO. Water is removed by coarsely ground magnesium perchlorate, CO_2 is injected to give a final concentration of 5% and the gas mixture is passed into a simple proportional counter. Details of counter, gas train and electronic equipment are given, with examples of the detection of the activity of labelled compounds of the long-chain fatty acid series. G. P. MITCHELL

4412. **Non-aqueous solvents in anion-exchange separations.** J. S. Fritz and D. J. Pietrzyk (Inst. for Atomic Res., Iowa State University, Ames, U.S.A.). *Talanta*, 1961, **8** (2–3), 143–162 (in English).—The distribution coefficients between Dowex-1 resin and various mixtures of HCl, H_2O and an organic solvent have been determined for Bi^{3+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Cr^{3+}, Cu^{2+}, Dy^{3+}, Fe^{3+}, La^{3+}, Mn^{2+}, Ni^{2+}, Sc^{3+}, Th^{4+}, UO_2^{2+}, VO^{2+}, Zn^{2+} and ZrO^{2+}. The solvents studied were acetone, dioxan, ethanediol, ethanol, isopropyl alcohol and methanol. Generally, the distribution coefficients were higher than in HCl - H_2O systems. The effectiveness of the alcohols decreased in the order isopropyl alcohol, ethanol, methanol. Procedures for the separation of several combinations of metals have been developed. R. M. ROWLEY

4413. **Ethanol - water - hydrochloric acid eluents in anion-exchange separations.** D. H. Wilkins and G. E. Smith (General Electric Res. Lab., Schenectady, New York, U.S.A.). *Talanta*, 1961, **8** (2–3), 138–142 (in English).—Some metal chloro-complexes that are only weakly adsorbed by anion-exchange resins from aq. HCl soln. are more strongly adsorbed from soln. containing ethanol. The distribution coefficients between Dowex-1 resin and a range of ethanol - H_2O - HCl compositions have been determined for Mn, La, Sc, Th and Y; Ca, Cr and Ni are only very weakly adsorbed, and can easily be separated from any of the other metals if a suitable solvent composition is chosen. If absolute ethanol is used as the solvent it is possible to separate Sc and Y. R. M. ROWLEY

4414. **Effect of the drying temperature on the ion-exchange properties of zirconium phosphate.** G. Alberti and A. Conte (Ist. Chim. Gen. ed Inorg. Lab. Chim. della Div. Geomineraria del C.N.R.N., Roma, Italy). *J. Chromatography*, 1961, **5** (3), 244–253 (in English).—Zirconium phosphate (PO_4^{3-} to Zr ratio 7:1) dried at 50° and at 260° is investigated as an ion-exchange medium for Na^+, K^+, Li^+, Cs^+, Rb^+, Tl^+, Ba^{2+}, Sr^{2+}, Th^{2+} and UO_2^{2+}. Studies of the ratios of mass distribution coefficients for monovalent ions on zirconium phosphate dried at these temperatures showed the ratios to decrease in the following order—Tl^+, K^+, Rb^+, Cs^+, Na^+, Li^+. Experimental column elutions and separations confirmed the results of these studies, since a number of separations, *e.g.*, Sr from Cs, and Li from Na, are easier when the material prepared at the higher temperature is used. Comparison is made with organic ion-exchangers and the phenomena observed with zirconium phosphate are explained on the assumption that condensation of the phosphate structure occurs at the higher temperature of preparation. G. P. MITCHELL

4415. **Apparatus for high-voltage paper electrophoresis.** D. Gross (Tate & Lyle Ltd., Keston, Kent, England). *J. Chromatography*, 1961, **5** (3), 194–206 (in English).—The high-voltage paper-electrophoresis equipment described can be operated at potentials in excess of 50 V per cm and an energy input of 1 W per sq. cm. To achieve this, special precautions have been taken to dissipate the heat energy produced. The heat exchangers consist of aluminium plates (22 in. × 13 in. × 1 in.), the surfaces of which are flat to within 0·001 in., and they are internally grooved to allow water coolant to circulate counterwise. Polythene film is used between the plates as an electrical insulator and the paper strip is clamped into position by a controlled uniform pressure, exerted on the top plate via an inflated air cushion. Experimental results show linear relationships between migration rates and voltage and time, with 100 V per cm applied potential and 1 W per sq. cm energy input, with a reproducibility of $\simeq 3\%$. This equipment can be used for separations of complex mixtures of low-molecular-weight compounds, *e.g.*, amines, amino-acids, sugars and inorganic cations, with a high degree of resolution in a short time. G. P. MITCHELL

4416. **Preparation and properties of acrylamide gel for use in electrophoresis.** S. Raymond and Y.-J. Wang (Pepper Lab., Univ. Pennsylvania, Philadelphia, U.S.A.). *Anal. Biochem.*, 1960, **1** (4–5), 391–396.—Acrylamide is a water-soluble monomer which dissolves completely in buffers over a wide range of pH and, except possibly at the ends of chains, the molecule has no free hydroxyl or acidic groups. It polymerises to a transparent, insoluble, flexible material which is suitable for gel electrophoresis, but which must be protected from evaporation and from overheating during the run. Suitable apparatus for preparing the gel and for carrying out the electrophoresis is described. F. POWELL

See also Abstract—**4030**, Applications of gas chromatography.

Optical

4417. **Application of the X-ray diffraction process in chemical analysis.** G. Menczel (L. Eötvös Sci. Univ., Budapest, Hungary). *Magyar Kém. Lapja*, 1961, **16** (3), 125–130.—A review of the application of the Debye - Scherrer method to qual. and quant. chemical analysis is given. (40 references.) B. VASZKO

4418. **Effect of composition of the powder on the results of spectrographic analysis by the insufflation method.** A. K. Rusanov and N. T. Batova (All-Union Sci. Res. Inst. of Mineral Raw Materials). *Zavod. Lab.*, 1961, **27** (3), 299–306.—Of various factors studied, one of the most important is particle size. The dimensions should be reduced to $< 0{\cdot}04$ mm. G. S. SMITH

4419. **Increasing the sensitivity of spectrographic determinations of rare elements in solutions.** Ya. D. Raĭkhbaum and E. S. Kostyukova (Irkutsk State Sci. Res. Inst. of Rare Metals). *Zavod. Lab.*, 1961, **27** (3), 306–309.—To reduce the concentration of water vapour in the discharge gap, thus increasing the intensity of excitation, the upper electrode consists of a capillary in a carbon rod. The soln. flowing through the capillary from a glass tube container gives a thin film on the electrode surface in the spark gap, and the evaporated water passes upwards away from the discharge. G. S. SMITH

4420. **Use of the compensation method in flame photometry.** D. N. Ivanov (V. V. Dokuchaeva Soil Inst., Acad. Sci., USSR). *Zavod. Lab.*, 1961, **27** (3), 297–299.—The scheme is based on the use of two compensated photo-elements (one for, say, Na and the other for, say, Ca). Errors due to interfering elements can be practically eliminated. Thus, with soil soln., if compensation for contents of Ca of 500 mg per litre has been obtained, the determination of Na in soln. containing between 0 and 1000 mg of Ca per litre can be accurately carried out. G. S. SMITH

4421. **Differential absorption spectrometer for the infra-red.** M. D. Sturge (Royal Radar Estab., Malvern, Worcs., England). *J. Sci. Instrum.*, 1961, **38** (3), 96–98.—The method described was designed for measuring the change in absorption coeff. due to the introduction of an impurity into a semiconductor. The specimen is in two halves which differ only in impurity content, and the beam is passed alternately through the two halves with a repetition frequency of 1 c/s. The detector output then consists of a signal at the chopping frequency of the incident beam (10 c/s) modulated by the 1 c/s signal. After rectification of the 10 c/s signal, the 1 c/s signal is amplified and rectified. A change of less than 10^{-3} cm^{-1} can be observed in the presence of substantial background absorption. G. SKIRROW

4422. **High-temperature infra-red cells for studies of high-polymer reactions.** W. A. Bishop (Copolymer Rubber & Chemical Corp., Baton Rouge, La., U.S.A.). *Anal. Chem.*, 1961, **33** (3), 456–459.—Equipment and techniques are described for studies of polymers deposited on, or sandwiched between, pressed potassium chloride discs. One cell, a thermostatically controlled heated type, is satisfactory from the standpoint of simplicity of construction, ease of handling and temperature control. The second cell permits the simultaneous monitoring of 10 film samples in extended, unattended runs. The use of these cells widens the application of infra-red spectrophotometry. C. B. BAINES

4423. **Fluorescence measurement.** E. J. Bowen (Phys. Chem. Lab., Oxford, England). *Photoelect. Spectr. Gr. Bull.*, 1961, (13), 331–333.—A brief review is given of the conditions under which fluorescence is observed and of the considerations which must be given to the presentation of measured fluorescence spectra. (6 references.) G. SKIRROW

4424. **Some observations on fluorimetric determinations.** H. Braunsberg and V. H. T. James (Dept. Chem. Path., St. Mary's Hospital Med. Sch., London, England). *Anal. Biochem.*, 1960, **1** (6), 443–451.—The variation of sensitivity with wavelength, the effect of slit width on spectral resolution, and the instrumental stability have been studied in a commercially available spectrofluorimeter (Aminco-Bowman). R. A. BRENAN

4425. **Fluorimetry. VI. The [quenching] effect of chloride ion on the fluorescence of quinine in aqueous solution and its dependence on acid concentration.** J. Eisenbrand and M. Raisch (Chem. Untersuchungsamt f. das Saarland, Saarbrücken, Germany). *Z. anal. Chem.*, 1961, **179** (5), 352–355 (in German).—Measurements were made on the effect of KCl (1 to 500mM) on the fluorescence of quinine (1μM) in the presence of H_2SO_4 or $HClO_4$ (0·001 to 10N). The exciting radiation was the mercury line at 366 mμ. The quenching coeff. (α) was calculated by setting the fluorescence of the soln. without KCl at 100 scale divisions on the galvanometer and expressing that of the test soln. as a fraction of this, correcting for a blank when necessary. The effect of acid is to diminish the quenching effect. With low KCl concn. (1 to 3mM), addition of acid up to 10N almost restored the original value (*i.e.*, $\alpha = \simeq 1$); $HClO_4$ was slightly more effective. With KCl concn. of $\simeq$ 100mM, when α without acid was almost zero, the addition of acid up to 10N gave $\alpha = \simeq 0{\cdot}3$. It is assumed that the quenching effect is due to Cl^-, and the partial reversal by acid to suppression of HCl ionisation or to ion-pair formation. The effect of acid is thus comparable to that of Hg.

VII. The influence of halide ions on the fluorescence of quinine sulphate and its dependence on salt concentration. J. Eisenbrand and M. Raisch. *Ibid.*, 1961, **179** (6), 406–409 (in German).—The quenching effects of Cl^-, Br^- and I^- on the fluorescence of 10^{-6}M-quinine sulphate in 0·01N-H_2SO_4 were compared. Experimental details were as described in Part VI. The anions have a progressively greater quenching effect in the order given, especially at higher concn. The quenching coefficient, α (= fluorescence of the test soln./fluorescence of halide-free soln.) falls to 0·045 for 0·1M-Cl^- and to 0·015 for 0·1M-I^-. Values of the quenching constant, K, $[= c\alpha/(1-\alpha)]$, where c is the concn. (millimoles per litre) of the halide ion, are $4{\cdot}7 \times 10^{-3}$ for Cl^-, $3{\cdot}2 \times 10^{-3}$ for Br^- and $2{\cdot}6 \times 10^{-3}$ for I^-. These are mean values, the actual figures varying somewhat with concn. The effects are interpreted in terms of dissociation of strong electrolytes and hydration of the anions. G. RUSSELL

4426. **Fluorescence excitation spectra and fluorescence sensitivity.** C. A. Parker (Admiralty Materials Lab., Holton Heath, Poole, Dorset, England). *Photoelect. Spectr. Gr. Bull.*, 1961, (13), 334–338.—A discussion is given of a method of compiling data of fluorescence sensitivities of different substances in such a way that the values are independent of the instruments used to measure them. The product $\phi\epsilon$ (ϕ is the fluorescence efficiency and ϵ is the molecular extinction coefficient of the solute at the frequency used for excitation) is a fundamental characteristic of the compound at the frequency chosen for excitation, and is a measure of its fluorescence sensitivity. G. SKIRROW

See also Abstract—**4033**, Operational statistics in emission spectrography.

Electrical

4427. **Construction of thermopiles from fine wire.** C. A. Glover and R. R. Stanley (Res. Lab., Tennessee Eastman Co., Kingsport, U.S.A.). *Anal.*

Chem., 1961, **33** (3), 477–478.—A simple, rapid method is described for the construction of 80-junction thermopiles from easily obtainable equipment for use in the ebulliometric determination of the number-average mol. wt. of polymers. (*Cf. Anal. Abstr.*, 1961, **8**, 4268.) C. B. BAINES

4428. **Investigation of *N*-methylacetamide as a non-aqueous polarographic solvent.** D. E. Sellers and G. W. Leonard, jun. (Dept. of Chem., Kansas State Univ., Manhattan, U.S.A.). *Anal. Chem.*, 1961, **33** (3), 334–336.—*N*-Methylacetamide is a satisfactory medium for polarographic studies of organic and inorganic substances. It has a high dielectric constant, is liquid from 29° to 206° and can be supported on tetraethylammonium bromide. A preconditioned mercury pool, with a reproducibility within 0·003 V, is a suitable reference electrode. Oxygen interference, moisture contamination and the effect of concn. on diffusion current are considered, and a list is given of compounds that produce well-defined polarograms, with their half-wave potentials and diffusion-current constants. C. B. BAINES

4429. **Influence of foreign electrolyte concentration in square-wave polarography.** F. von Sturm and M. Ressel (Res. Lab., Siemens-Schuckertwerke A.-G., Erlangen, Germany). *Microchem. J.*, 1961, **5** (1), 53–65.—Examples are given of a number of polarographically reversible and irreversible reductions that were recorded by means of a Mervyn Harwell square-wave polarograph, with a frequency of 225 c/s and a square-wave amplitude of 32 mV. It is shown that a considerable increase in the sensitivity of irreversible reactions can be obtained, without the indication of reversible reactions being impaired, if solutions of low foreign-electrolyte content are used. I. A. SIMPSON

4430. **New electrode for oscillographic polarography.** K. Micka (Polarographic Inst., Acad. Sci., Prague, Czechoslovakia). *Chem. Listy*, 1961, **55** (4), 474–477.—The properties of a new electrode formed from a mercury drop suspended on the end of an isolated silver wire are compared with those of other electrodes used in oscillographic polarography. J. ZÝKA

4431. **Applications of cathode-ray polarography in the field of oceanography.** G. C. Whitnack (Chem. Div., U.S. Naval Ordnance Test Sta., China Lake, Calif.). *J. Electroanal. Chem.*, 1961, **2** (2), 110–115 (in English).—The single-sweep cathode-ray polarograph (Polarotrace K–1000) (*cf.* Reynolds and Davis, *Analyst*, 1953, **78**, 314) has been applied to the determination of Cu^{2+}, Co^{2+}, Zn^{2+} and Mn^{2+} in sea water at concn. as low as 5×10^{-8} g per ml, the determination of dissolved O and, by means of a silver - silver chloride electrode system, the concn. of Cl^-.

T. R. ANDREW

4432. **Electrodes for pH measurements.** R. G. Bates (Nat. Bureau of Standards, Washington, D.C., U.S.A.). *J. Electroanal. Chem.*, 1961, **2** (2), 93–109 (in English).—A review of the behaviour of hydrogen, quinhydrone, antimony and glass electrodes is given. Tables are given of corrections for the effect of pressure on the hydrogen electrode and for salt errors of the quinhydrone electrode, and of the corrections to be applied to 12 commercial glass electrodes when used in alkaline soln. (0·1M- and 1·0M-NaOH). T. R. ANDREW

4433. **Linear chrono-amperometric determinations with electrochemical indicators. The indicating mercury electrode in titrations with EDTA.** M. Moratille and B. Trémillon (Lab. Chim. Anal., École de Phys. et Chim., Paris). *Bull. Soc. Chim. France*, 1961, (3), 506–510.—The technique of linear chrono-amperometry consists in plotting current against potential or time when a potential, increased linearly with time, is applied to a cell in which an electrochemical reaction takes place at a stationary electrode in an undisturbed soln. With a buffered soln. of EDTA and a mercury electrode a wave is obtained the height of which is proportional to the concn. of EDTA. The procedure can therefore be adapted to the determination of metals that form stable complexes with EDTA, the excess of EDTA being determined. It has been used to determine μg amounts of Ca^{2+}.

G. BURGER

4434. **Chronopotentiometric transition times and their interpretation.** W. H. Reinmuth (Dept. of Chem., Columbia Univ., New York 27, U.S.A.). *Anal. Chem.*, 1961, **33** (3), 322–325.—A discussion is given of chronopotentiometric processes in which charge transfer is preceded by adsorption or chemical kinetic complications. Various mechanisms are distinguished by the use of certain diagnostic criteria, and implications in the field of analytical procedures are considered. C. B. BAINES

4435. **Theory and applications of the chronopotentiometric method with imposed current proportional to the square root of the time. I. General introduction and the case of reactions of direct discharge.** H. Hurwitz and L. Gierst (Lab. de Chim. Anal., Fac. Sci., Univ. Libre de Bruxelles, Belgium). *J. Electroanal. Chem.*, 1961, **2** (2), 128–141 (in French).—The basic equipment for the chronopotentiometric method has been slightly modified to permit the continuous variation of current with time according to the equation $i = \rho\sqrt{t}$, where ρ is the amplitude factor. Several circuits are given permitting variations on this fundamental principle. The main advantage claimed for this technique is that the time elapsed at the end-point is directly proportional to the initial concn. of the reacting constituent of the soln. The diffusion to a plane mercury surface is deduced from Fick's law and examples are given of the use of the technique for reversible and irreversible systems.

II. Case of reactions of direct discharge in spherical and cylindrical diffusion systems. H. Hurwitz. *Ibid.*, 1961, **2** (2), 142–151.—The calculations made in Part I for diffusion to a plane surface are extended to cover diffusion to a sphere and to a cylinder, and the method may be applied with a hanging-drop mercury electrode or a wire electrode.

T. R. ANDREW

4436. **Redoxokinetic and impedance titrations: new analytical techniques.** K. S. Narayanan and H. C. Gaur (Central Electrochem. Res. Inst., Karaikudi, India). *J. Electroanal. Chem.*, 1961, **2** (2), 161–165 (in English).—The technique of Doss *et al.* (*Electrochim. Acta*, 1959, **1**, 22) has been applied successfully to the titration of Fe^{II} with

vanadate and of ferrocyanide with Pb^{II}. Measurement of the cell impedance is also suitable as a means of end-point detection. A circuit diagram of the apparatus is given. T. R. ANDREW

4437. **The "multiple" process for colorimetric ultra-micro titration with photo-electric end-point detection. I.** J. Mika and B. Szopory (Tech. Univ., Miskolc, Hungary). *Magyar Kém. Foly.*, 1961, **67** (3), 129–137.—The coloured soln. containing the component to be determined is contained in a capillary cell (length 30 mm, diameter 3 mm) and a blank soln. is contained in a larger cell (length 30 mm, diameter 45 mm). The two cells are placed in an instrument in which the extinctions are compared by means of a photocell or photomultiplier device. To perform a determination, a standard soln. containing a known concn. of the test substance is added to the blank soln. from a microburette (delivering reproducibly to 0·001 ml) until the extinctions of the two cells are identical. Thorough mixing of the soln. during titration is essential. In a quoted example, 1 μg of Cr^{VI} can be determined as chromate in 0·5 ml of soln. with a relative error of ± 0·71%. Results by the new method are compared with those by conventional colorimetric procedures; with very dilute or very concentrated soln., to which the Beer - Lambert law does not apply, the new method is often superior to conventional procedures. Constructional details of the apparatus are given. (*Cf. Mikrochim. Acta*, 1960, 729; *Anal. Abstr.*, 1961, **8**, 1770.) B. VASZKO

4438. **Simple amplifier and pulse-height analyser for an X-ray scintillation counter.** B. B. Trott (Viriamu Jones Lab., Univ. Coll., Cardiff, Wales). *J. Sci. Instrum.*, 1961, **38** (3), 74–77.—Circuit details are given of a simple four-valve amplifier and pulse-height analyser for a counter consisting of a thallium-activated sodium iodide crystal mounted on an E.M.I. type 952B photomultiplier. Large noise pulses in the photomultiplier are thought to be caused by repeated optical feed-back. G. SKIRROW

4439. **A simple efficient liquid scintillator for counting aqueous solutions in a liquid scintillation counter.** G. A. Bray (Nat. Heart Inst., Bethesda, Md., U.S.A.). *Anal. Biochem.*, 1960, **1** (4–5), 279–285.—A liquid scintillator is described containing naphthalene (60 g), 2,5-diphenyloxazole (4 g), 1,4-di-2-(5-phenyloxazolyl)benzene (0·2 g), methanol (100 ml) and ethanediol (20 ml), diluted to 1 litre with dioxan. In the presence of 1 ml of water the efficiency for ^{14}C is 65·6% and for tritiated water 11·7%. This liquid scintillator has been used to count ^{14}C and ^{3}H in urine, plasma and liver homogenate. The effects of isotope concn., solute concn., and the presence of acids and bases have been investigated. The effect of protein precipitants and the elimination of the quenching effect of urinary pigment have also been studied. F. POWELL

4440. **A solids-inlet system for a mass spectrometer.** H. E. Lumpkin and G. R. Taylor (Res. and Devel. Div., Humble Oil and Refining Co., Baytown, Tex., U.S.A.). *Anal. Chem.*, 1961, **33** (3), 476–477.—An all-glass apparatus is described which can be heated to about 500° and which allows low-vapour-pressure solid materials to be introduced without breaking the vacuum. The spectra of terephthalaldehyde, terephthalaldehydic acid and terephthalic acid are given as examples of the use of the system. C. B. BAINES

See also Abstracts—**4051**, Oscillographic polarography with hanging-drop mercury electrode. **4145**, Coulometric analyser for O. **4255**, Apparatus for air content of oil.

ERRATA

February (1961) issue, abstract 758, line 2. *For* Berquist *read* Bergquist.
April (1961) issue, abstract 1675, line 3. *For* Guiseppe *read* Giuseppe.
May (1961) issue, abstract 1895, line 4. *For* Pelzulayev *read* Pelzulaev.
Abstract 2156, line 2. *For* F. de Francesco *read* F. De Francesco.
July (1961) issue, abstract 2916, line 2. *For* Bártfai *read* Bártfay.
Abstract 2916, line 3. For *Magyar Kém. Foly.* read *Magyar Kém. Lapja.*
August (1961) issue, abstract 3172. *Insert* except Fe *after* cations.
Abstract 3321, line 5. *For* 1960 *read* 1961.
Abstract 3461, line 6. *For* 0·2 to 0·6% *read* 0·0004 to 0·0056%.
September (1961) issue, abstract 3560, 2nd column, line 45. *For* Korodán *read* Korondán.
Abstract 3562, 2nd column, line 17. *For* Freidrich *read* Friedrich.
Abstract 3678, line 6. *For* 1 g *read* 1 μg.
Abstract 3805, line 12. *For* 1·0N-$(NH_4)_2SO_4.Fe_2(SO_4)_3$ *read* 0·1N-$(NH_4)_2SO_4.Fe_2(SO_4)_3$.
Abstract 3815. The last line should read "The relative error is usually < 5% for 0 to 5 p.p.m."
Abstract 3869. Line 9 should read "determined with a coeff. of variation of 3% or greater".
Cross references after abstract 3977, line 5. *For* Cu *read* Ca.

ABBREVIATIONS

Certain abbreviations in everyday use are not included in the following list. When any doubt might arise from the use of an abbreviation or symbol the word is printed in full.

alternating current	a.c.
ampere	amp.
Ångström unit	A
anhydrous	anhyd.
approximate, -ly	approx.
aqueous	aq.
atmospher-e, -ic	atm.
boiling-point	b.p.
British thermal unit	B.Th.U.
calorie (large)	kg-cal.
calorie (small)	g-cal.
centimetre	cm
coefficient	coeff.
Colour Index	C.I.
concentrated	conc.
concentration	concn.
constant	const.
crystalline / crystallised	cryst.
cubic	cu.
current density	c.d.
cycles per second	c/s
density	ρ
density, relative	d or wt. per ml
dilute	dil.
direct current	d.c.
distilled	dist.
electromotive force	e.m.f.
equivalent	equiv.
ethylenediaminetetra-acetic acid	EDTA
gram	g
gram-molecule	mole
half-wave potential	$E_{\frac{1}{2}}$
hour	hr.
hydrygen ion exponent	pH
infra-red	i.r.
insoluble	insol.
international unit	i.u.
kilogram	kg
kilovolt	kV
kilowatt	kW
liquid	liq.
maxim-um, -a	max.
melting-point	m.p.
microgram	μg (not γ)
microlitre	μl
micromole	μmole
micron	μ
milliampere	mA
milli-equivalent	milli-equiv.
milligram	mg
millilitre	ml
millimetre	mm
millimicrogram	mμg
millimolar	mM
millivolt	mV
minute (time)	min.
molar (concentration)	M
molecul-e, -ar	mol.
normal (concentration)	N
optical rotation	α_l
ounce	oz
parts per million	p.p.m.
per cent.	%
per cent. (vol. in vol.)	% (v/v)
per cent. (wt. in vol.)	% (w/v)
per cent. (wt. in wt.)	% (w/w)
potential difference	p.d.
precipitate (as a noun)	ppt.
precipitated	pptd.
precipitating	pptg.
precipitation	pptn.
preparation	prep.
qualitative, -ly	qual.
quantitative, -ly	quant.
recrystallised	recryst.
refractive index	n_λ^t
relative band speed	R_F
relative humidity	r.h.
revolutions per minute	r.p.m.
saponification value	sap. val.
saturated calomel electrode	S.C.E.
second (time)	sec.
soluble	sol.
solution	soln.
specific gravity	sp. gr.
specific rotation	$[\alpha]_\lambda^t$
square centimetre	sq. cm
standard temp. and pressure	s.t.p.
temperature	temp.
ultra-violet	u.v.
vapour density	v.d.
vapour pressure	v.p.
volt	V
volume	vol.
watt	W
wavelength	λ
weight	wt.

In addition, the following symbols may be used in conjunction with numerical values or in mathematical expressions—

greater than	$>$	less than	$<$
not greater than	$\ngtr$	not less than	$\nless$
is proportional to	$\propto$	of the order of, approximately	$\simeq$

The principal Pharmacopoeias are denoted by B.P., U.S.P. or D.A.B., together with the identifying roman numeral or year.

Valency states are represented by a superscript roman numeral, *e.g.*, Fe^{II}, Mo^{V}. Substances in the ionic state are represented by Na^+, Fe^{2+}, Fe^{3+}, etc., for cations and by Cl^-, SO_4^{2-}, PO_4^{3-}, etc., for anions.

The chemical nomenclature used in the abstracts is that recommended by The Chemical Society ("Handbook for Chemical Society Authors", The Chemical Society, London, 1960), and may differ from that used in the original articles.

Volume 8. No. 10, Abstracts 4029 – 4440 October, 1961

ANALYTICAL ABSTRACTS

A PUBLICATION OF
THE SOCIETY FOR ANALYTICAL CHEMISTRY

EDITORIAL COMMITTEE

Chairman: B. A. Ellis

Members: B. S. Cooper, C. H. R. Gentry, C. A. Johnson, H. F. W. Kirkpatrick, B. J. Walby, W. A. Waygood, K. A. Williams
and
President of the Society: A. J. Amos

Hon. Secretary of the Society
R. E. Stuckey

Hon. Treasurer of the Society
D. T. Lewis

Editor: Norman Evers, B.Sc., Ph.D., F.R.I.C.

Assistant Editor: Mrs. H. I. Fisk, B.Sc.

CONTENTS

	Abstract
General Analytical Chemistry	
Reviews; reagents; methods of general application	4029
Inorganic Analysis	
General methods; elements (in order of the Periodic Table); minerals; industrial products	4044
Organic Analysis	
Elements and radicals; organic compounds; industrial products	4199
Biochemistry	
BIOLOGICAL FLUIDS; ANIMAL AND VEGETABLE TISSUES	4274
PHARMACEUTICAL ANALYSIS	4324
FOOD	
Food additives; beverages; edible oils and fats; vitamins	4346
SANITATION	
Air; water; sewage; industrial wastes	4374
AGRICULTURAL ANALYSIS	
Soil; fertilisers; herbicides; pesticides; animal feeding-stuffs	4381
General Technique and Apparatus	
GENERAL	4391
CHROMATOGRAPHY; ION EXCHANGE; ELECTROPHORESIS	4403
OPTICAL	4417
ELECTRICAL	4427

Printed and published for the Society for Analytical Chemistry by W. Heffer & Sons Ltd., Cambridge, England.
Communications to be addressed to the Editor, Norman Evers, 14, Belgrave Square, London, S.W.1.
Enquiries about advertisements should be addressed to Walter Judd Ltd., 47, Gresham Street, London, E.C.2.
Entered as Second Class at New York, U.S.A., Post Office.